



Facile stripping voltammetric determination of haloperidol using a high performance magnetite/carbon nanotube paste electrode in pharmaceutical and biological samples



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ABSTRACT

Multi-walled carbon nanotubes decorated with Fe₃O₄ nanoparticles were prepared to construct a novel sensor for the determination of haloperidol (Hp) by voltammetric methods. The morphology and properties of electrode surface were characterized by scanning electron microscopy (SEM) and electrochemical impedance spectroscopy. This modified sensor was used as a selective electrochemical sensor for the determination of trace amounts of Hp. The peak currents of differential pulse and square wave voltammograms of Hp increased linearly with its concentration in the ranges of 1.2×10^{-3} – 0.52 and 6.5×10^{-4} – $0.52 \mu\text{mol L}^{-1}$, respectively. The detection limits for Hp were 7.02×10^{-4} and $1.33 \times 10^{-4} \mu\text{mol L}^{-1}$ for differential pulse and square wave voltammetric methods, respectively. The results show that the combination of multi-walled carbon nanotubes and Fe₃O₄ nanoparticles causes a dramatic enhancement in the sensitivity of Hp quantification. This sensor was successfully applied to determine Hp in pharmaceutical samples and biological fluids. The fabricated electrode showed excellent reproducibility, repeatability and stability.

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1. Introduction

Hp is an antipsychotic drug most widely used in the treatment of schizophrenia and acute psychotic states and delirium. It is also used in the control of the symptoms of acute psychosis, such as drug-induced psychosis, psilocybin, amphetamines, ketamine, phencyclidine and psychosis associated with high fever or metabolic disease [1–3]. Accurate measurements of antipsychotic drug levels will also facilitate more precise estimates of dopamine D₂ receptor occupancy, a factor that has been suggested to serve as a cross-species guideline for deriving clinically relevant antipsychotic doses for animal models [4]. Since the antipsychotic drugs are very active, they are usually administered at low daily dosages [5]. At steady state these doses result in plasma levels in the low ng mL^{−1} range. In order to quantify the levels of Hp, an analytical method with high sensitivity is required [5]. The analytical methods for the determination of Hp and its metabolites in biological samples so far reported include gas chromatography (GC), GC–mass spectrometry (MS), high-performance liquid chromatography (HPLC), HPLC–MS, capillary electrophoresis, etc. [2,5–8]. These methods usually involve time-consuming multi-step pretreatment including liquid–liquid extraction and/or solid-phase extraction to remove impurities contained in plasma or serum for the detection of these species. Also,

these methods are expensive and not suitable for in-situ analysis due to the ponderous and complicated instruments [5–8]. That is why, the development of simple, accurate, selective, fast and cheap method for the determination of Hp in biological fluids and pharmaceutical samples appeared at present to be an attracted case.

On the contrary, the electrochemical methods as alternative of these techniques have been accepted as the efficient methods to determine drugs due to their excellent sensitivity, short analysis time, portability, low cost and low maintenance [9,10]. Voltammetric methods using mercury electrodes have suggested for the determination of Hp [11–13]. However, in order to avoid the environmental pollution and health hazard caused by traditional mercury electrodes, and some inconveniences complicating the use of voltammetry by them, various mercury-free electrodes (carbonaceous electrodes) have been developed over the past years [14,15].

Adams first introduced carbon paste as the electrode material [16]. Carbon paste, which is a mixture of carbon powder and a suitable liquid binder, represents the most flexible substrate for a wide variety of chemical and biological modifications. Application of chemically modified electrodes (CMEs) in the electrochemical determinations has been widely considered as a sensitive and selective analytical method for the determination of trace amounts of important species [16–19]. The operation mechanism of such chemically modified carbon paste electrodes (CMCPes) depends on the properties of the modifier used to improve selectivity and sensitivity towards the target species. When the experimental condition is optimized, this approach

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eliminates the problem of interferences by other species in the sample [16–19].

The key point to obtain a good and reliable CME is the kind of materials that constitute the modified electrode. The attractive properties of nanomaterial have paved the way for the fabrication of a wide range of modified CPEs that exhibit improved analytical capacities. Multi-walled carbon nanotubes (MWCNTs) as a type of highly conductive nanomaterials, provide excellent performance in enhancing electrochemical reactivity, promoting electron-transfer reactions and alleviating surface fouling [20–22]. The functionalization of MWCNTs has resulted in various nanocomposite materials with many new properties. Nanocomposite materials have been increasingly important in electrochemical researches [17–20]. Nanoparticle hybrid materials made from inorganic solids and MWCNTs are highly promising for applications in nanoscale devices and nanoelectronics. Furthermore, uniformly dispersed nanoparticles on MWCNT surfaces yield highly effective sensing layer for CMEs. Fe_3O_4 nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) have attracted an increasing interest in construction of sensors and biosensors because of their good biocompatibility, strong super paramagnetic property, low toxicity, easy preparation and high adsorption ability. Moreover, $\text{Fe}_3\text{O}_4\text{NPs}$ exhibit high surface area and low mass transfer resistance [23,24]. Therefore, the decoration of MWCNTs with Fe_3O_4 magnetic nanoparticles can provide excellent electrochemical platforms for Hp analysis due to the combination of the enlarged active surface area, strong adsorptive capability of the nanomaterial and their specific interaction ability.

To the best of our knowledge, no study has reported the determination of Hp using carbon paste electrodes. The works published in the literature report the determination of Hp with mercuric and glassy carbon electrodes (Table 1). So, in this study we described the preparation and suitability of $\text{Fe}_3\text{O}_4\text{NPs}/\text{MWCNTs}/\text{CPE}$ as a new electrode for the determination of Hp. The usefulness of the modified electrode with improved sensitivity, selectivity and accuracy has been demonstrated for the applications in the pharmaceutical samples and biological fluids.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used in this work were of analytical grade and used as received without further purification. Haloperidol (United States Pharmacopeia (USP) Reference Standard) was purchased from Fluka. MWCNTs were purchased from Nanostructured & Amorphous Materials (Houston, TX, USA). Graphite powder (with a particle size less than 1 μm) and paraffin oil were purchased from Aldrich. All aqueous solutions were prepared with doubly distilled deionized water (DDW). Britton–Robinson (B–R) universal buffers (pH 4.5–8.5) were prepared in DDW and were tested as supporting electrolytes.

2.2. Apparatus

All electrochemical experiments including cyclic voltammetry (CV) and differential pulse voltammetry (DPV) and square wave voltammetry (SWV) were performed using a Metrohm instrument (Swiss), Model 797 VA Computrace. A conventional three-electrode system was used

with a carbon-paste working electrode (unmodified or modified), a saturated Ag/AgCl reference electrode and a Pt wire as the counter electrode (Azar electrode, Iran). All potentials reported are vs. Ag/AgCl. A pH-meter, Model 713 (Metrohm, Swiss), was used to determine pH values of the solutions. The structure of the prepared electrodes was characterized by a scanning electron microscope (SEM-EDX, XL30 and Philips Nederland). The HPLC was used (Agilent 1100, USA).

2.3. Preparation of $\text{Fe}_3\text{O}_4\text{NPs}/\text{MWCNTs}$

Chemical pretreatment is a simple and effective way to introduce oxygen groups (COOH , $\text{C}=\text{O}$ and OH) onto the MWCNT surface for improving their properties. They were purified and functionalized as described elsewhere [17,25]. Briefly, a 500 mg of the MWCNTs was heated in an oven under a temperature of 400 $^\circ\text{C}$ in nitrogen atmosphere for 2 h. Then MWCNTs were dispersed in 50 mL of 6.0 M HCl for 2 h under ultrasonic agitation under the nitrogen atmosphere; filtered on a Watman 42 filter paper and washed with DDW until the pH of the solution was neutral. These MWCNTs were dried under the IR lamp. Open-end MWCNTs with hydrophilic surfaces were thus obtained.

Iron oxide–MWCNT composite was prepared according to a previously reported method with some modification [26]. For this purpose, 50.0 mg of functionalized MWCNTs was added into 30 mL of distilled water by ultrasonic irradiation for 20 min. Then 40.0 mg of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added under stirring. After the mixture was stirred vigorously for 30 min under N_2 atmosphere, 60.0 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added and kept stirring under N_2 atmosphere for 30 min. 4 mL of concentrated ammonia solution diluted with 20 mL of distilled water was added into the mixture drop by drop. Then the solution was filtered on a 0.65 μm filter membrane and washed with distilled water repeatedly. The resulting product was dried overnight at 100 $^\circ\text{C}$ in an oven under nitrogen atmosphere. The sample was then annealed at 250 $^\circ\text{C}$ for 1 h and 650 $^\circ\text{C}$ for 2 h in a steam of nitrogen.

2.4. Electrode preparation

CPE was prepared by hand-mixing graphite powder and paraffin oil with 70/30 (w/w) in a mortar with a pestle. A portion of the composite mixture was packed firmly with a piston-driven carbon paste electrode holder. For preparing a modified electrode, graphite powder and 20.0 mg portion of the $\text{Fe}_3\text{O}_4\text{NPs}/\text{MWCNT}$ were dispersed in 10 mL dimethylformamide (DMF) and homogenized ultrasonically for 10 min to increase the reproducibility after each electrode surface polishing. The mixture was stirred by a magnetic stirrer till the solvent evaporated completely. Then, paraffin oil was added to the mixture. This mixture was mixed in a mortar for at least 20 min to produce the uniform paste. The paste was carefully packed into the body tip to avoid possible air gaps, which often enhance the electrode resistance. When needed, the surface of carbon paste was mechanically renewed by extruding ca. 0.5 mm of carbon paste out of the electrode holder and smoothed with a paper. Usually, this simple operation was made before starting a new set of experiments.

Table 1
Comparison of some figures of merit of suggested electrodes for the determination of Hp.

Electrode	Method	Linear range ($\mu\text{mol L}^{-1}$)	Detection limit ($\mu\text{mol L}^{-1}$)	Ref.
Hanging mercury drop electrode (HMDE)	DPV	1–100	2.66	[11]
HMDE	SWV	1×10^{-3} –1.5	3.83×10^{-4}	[12]
HMDE	SWV	2.49×10^{-1} –3.38	4.75×10^{-3}	[13]
Glassy carbon	DPV	5.3×10^{-3} – 2.6×10^{-2}	1.3×10^{-3}	[14]
MWCNT-modified glassy carbon	CV	1.0×10^{-1} –25.0	8.0×10^{-3}	[15]
$\text{Fe}_3\text{O}_4\text{NPs}/\text{MWCNTs}/\text{CPE}$	SWV	6.5×10^{-4} –0.52	1.33×10^{-4}	This work
	DPV	1.2×10^{-3} –0.52	7.02×10^{-4}	

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