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Novel multi walled carbon nanotubes/β-cyclodextrin based carbon paste electrode for flow injection potentiometric determination of piroxicam

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ABSTRACT

A novel carbon paste electrode based on functionlized multi-walled carbon nanotubes/β-cyclodextrin composite (FMWCNTs/β-CD-CPE) is described for potentiometric determination of piroxicam (PXM). Improved sensitivity and selectivity was achieved by application of CDs as molecular host–guest recognition elements and MWCNTs. The electrochemical performance of carbon paste electrodes incroporated with FMWCNTs/β-CD composite was compared to those incroporated with MWCNTs and free CDs. Matrices compositions of each electrode are optimized on the basis of nature and content of the modifier, ionic sites and selected plasticizer. CPEs containing FMWCNTs/β-CD composite, hyamine (Hy) and 2-fluorophenyl 2-nitrophenyl ether (*f*-NPE) as electrode plasticizer, work satisfactory in the concentration range from 10^{-6} to 10^{-2} mol L^{-1} with Nernstain compliance (58.7 ± 0.9 mV $decade^{-1}$ activity) with fast response time of about 2 s and exhibit adequate operational lifetime (16 weeks). The developed electrodes have been applied for the potentiometric determination of PXM in pharmaceutical formulation under batch and flow injection analysis (FIA). FIA allows the analysis of 120 samples h^{-1} with the advantage of simplicity, accuracy and automation feasibility.

1. Introduction

Piroxicam (PXM, 4-hydroxy-2-methyl-N-(pyridine-2-yl)-2H-1, 2-benzo-thiazine-3-carboxamide-1,2-dioxide) is a well-known non-steroidal anti-inflammatory and analgesic drug (NSAIDs) for treatment of rheumatoid arthritis, osteoarthritis, ankylosing spondylitis and acute pain [1,2]. Data on reported techniques [3] for PXM determination in various objects are mainly based on chromatographic and spectrophotometric techniques, though voltamperometric and electrophoretic methods were also encountered. Nevertheless, most of these methods require expensive apparatus or involve several manipulation steps before the final result of analysis. An interest has been increased for developing reliable rapid and accurate procedures for PXM quantification.

Potentiometric methods are of choice since they possess the advantages of simplicity, accuracy without the need of separation or pretreatment procedures and the common availability of the instrumentation. Although a considerable attention has been given for drug analysis using ion-selective electrodes (ISEs) [4,5]; only a polyvinyl chloride (PVC) sensors based on ion-pair associates of PXM with tricaprylmethylammonium chloride [6] or Rhodamine 6 G [7] were found in literature. Potentiometric sensors based on ion-pairs are generally plagued by limited selectivity and their applications are restricted to more challenging matrices; therefore more selective molecular recognition component is clearly required. The beauty of electrochemical techniques is to utilize tailor made chemically modified electrodes (CMEs) for improved sensitivity and selectivity of the analytical applications [8,9]. Different types of molecular recognition elements have been proposed including; crown ethers, calixarenes, cyclodextrins (CDs) or porphyrins, and CDs were by far the most commonly used. Cyclodextrins are naturally occurring macrocyclic oligosaccharides formed of 1,4-glucosidic bond linked D (+) glucopyranose oligomers of 6, 7, and 8 glucose units yielding α-, β-, and γ-CDs, respectively [10]. CDs can form inclusion complexes with different types of guests without the formation of chemical bonds or changing their structure, where the binding forces are attributed to number of factors, such as hydrophobic forces, hydrogen bonding, size of the cavity and shape of the guest molecule [11,12]. Such unique properties introduced CDs as a sensing material in potentiometric sensors for many pharmaceutically important drugs [13–15].

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PVC membrane sensors still have certain inherent limitations as they are mechanically complicated, have short lifetime and difficult to be miniaturized. To overcome the aforementioned limitations, carbon paste electrodes (CPEs); mixture of carbon powder and a suitable binder, have been developed and introduced as an alternative to PVC sensors. CPEs possess the advantages of simple fabrication and regeneration process, fast response time and low Ohmic resistance [16]. The feasibility of sensing materials incorporation during mixing of paste results in the so-called modified carbon paste electrode (CMCPEs) with desired composition and pre-determined properties [17–19].

An important milestone in the history of carbon is the discovery of carbon nanotubes (CNTs) as one of the most important materials of the 21st century [20]. CNTs represent a novel class of carbon family with superior in terms of reaction rates and reversibility. The research in the field of sensors based on CNTs is still a hot topic and a number of excellent review articles have been published [21–26]. Concerning CPEs, many reports indicated that addition of CNTs to the electrode matrix improves the conductivity and, therefore, conversion of the chemical signal to an electrical signal [27–30].

Furthermore, defects in the graphite structure, at both end and side walls of CNTs, enables the functionalization via either covalent or noncovalent modifications. Functionalization of CNTs with macromolecular structures will lead to new composite materials possessing the properties of each component, or even with a synergistic effect, which would be useful in the fields of electrometric sensing [30–32].

To the best of our knowledge, no potentiometric CPEs incorporated with MWCNT/CD composite and PVC membrane plasticizers as binding material were found in literature. Taking into consideration the electrochemical properties of both CNTs and CDs, this work suggested a novel strategy for fabrication of potentiometric sensors for various analytical applications.

2. Experimental

2.1. Reagents

All reagents were of the analytical grade and double distilled water was used throughout the experiments. Cyclodextrin derivatives including, heptakis (2,6-di-O-methyl)-β-CD (**I**, Aldrich), heptakis (2,3,6-tri-O-methyl)-β-CD (**II**, Aldrich), 2-hydroxypropyl-β-CD (**III**, Aldrich), β-CD (**IV**, Sigma), α-CD (**V,** Aldrich) and γ-CD (**VI,** Aldrich) were tested as sensing ionophores.

Different ionic sites were incorporated in the electrode matrices namely; hyamine®1622 (Hy, Fluka), cetylpyridinium chloride (CPCl, Fluka), hexadecyltrimethylammonium bromide (HTMABr, Fluka), tri-dodecyltrimethylammonium bromide (TDTMABr, Sigma), didodecyl-dimethylammonium bromide (DDMABr, Fluka) and Septonex (Hlohovec, CZ).

2-nitrophenyl octyl ether (NPOE, Fluka), 2-fluorophenyl 2-nitrophenyl ether (*f*-NPE, Fluka), dioctylphthalate (DOP, BDH), dioctylsebacate (DOS, Avocado), tricresylphosphate (TCP, Fluka), and paraffin oil (Fluka) were used as paste binder. Graphite powder (synthetic 1–2 μm, Aldrich) and multiwall carbon nanotube (Aldrich) were applied as electrode materials.

2.2. Authentic samples

Authentic piroxicam sample, assigned to be 99%, was obtained from National Organization of Drug Control and Research, Giza, Egypt. Stock solution (10^{-2} molL^{-1}) was prepared by dissolving a weighed amount of PXM in 5×10^{-2} molL^{-1} sodium hydroxide solution and kept at 4 °C.

2.3. Pharmaceutical preparations

Dispercam® tablets (MUP, Cairo, Egypt, 20 mg/tablet) were purchased from local drug stores. Ten tablets were weighed, grinded, dissolved in 5×10^{-2} molL^{-1} sodium hydroxide solution, filtered off and completed to 50 mL with the same solution.

2.4. Apparatus

Potentiometric measurements were carried out using a 692-pH meter (Metrohm, Herisau, Switzerland, Art.no. 1.691.00100) with Ag/AgCl double-junction reference electrode (Metrohm, Art.no. 6.0726.100) and combined pH glass electrode (Metrohm, Art.no. 6.0202.100). Single line flow injection system was composed of four channel peristaltic pump (MCP Ismatec, Zurich, Switzerland), sample injection valve (ECOM, Ventil C, Czech Republic) and wall jet flow cells adapted for CPEs [33]. The change of electrode potential was monitored using 46-Range Digital Multimeter (Radioshack) with PC interface. Surface structure and FTIR studies were performed using JXA-840A electron probe microanalyzer (JEO-Japan) and Jasco FT/IR-6100 type A spectrophotometer (Tokyo, Japan), respectively.

2.5. Procedures

2.5.1. Preparation of FMWCNT/β-CD composite

MWCNTs were functionalized prior to composite preparation via introducing of carboxylic acid moieties onto its surface through oxidation in acidic medium. Carbon nanotubes were dispersed in 2.0 mol L^{-1} nitric acid solution for 24 h at 25 °C, washed afterwards with deionized water and dried at 75 °C [34]. The obtained functionalized carbon nanotube (FMWCNTs) were grinded with β-CD in agate mortar and pestle with the dropwise addition of ethanol over the first 10 min, followed by further grinding for 3 h. After drying, a black product was obtained and characterized via FTIR and electronic microscope.

2.5.2. Sensor construction

Carbon paste electrodes were fabricated by hand mixing of defined amounts of graphite powder, binder and modifier (Table 1), and the paste matrices were packed into a piston driven Teflon holder [18]. The resulting CPEs were conditioned in 10^{-3} mol L^{-1} PXM solution for 2 h before measurements and electrode surface regeneration was performed by screwing the piston and polishing with a wet smooth paper.

Table 1
Optimal composition of PXM carbon paste electrodes.

Electrode	Matrix composition
FMWCNT/ β-CD-CPE	2.50 mg FMWCNT/β-CD+1.25 mg Hy+97.5 mg graphite powder+60.0 μ L *f*-NPE
MWCNT-CPE	1.25 mg β-CD (**II**)+1.25 mg Hy+25.0 mg MWCNTs+75.0 mg graphite powder+90.0 μ L *f*-NPE
Graphite-CPE	1.25 mg β-CD (**II**)+ 1.25 mg Hy+100.0 mg graphite powder+40.0 μ L *f*-NPE