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Ibuprofen analysis in blood samples by palladium particles-impregnated sodium montmorillonite electrodes: Validation using high performance liquid chromatography

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ABSTRACT

The electrochemical detection of ibuprofen has been studied on Palladium-Montmorillonite (Mt) modified carbon paste electrode using differential pulse voltammetry. The optimization of the modifier preparation and the instrumental parameters was investigated. The results indicate that ibuprofen oxidation was favored in the presence of Pd–PdO particles. The quantitative determination of ibuprofen was statistically analyzed and validated using HPLC method. The detection and quantification limits, specificity and precision were found to be acceptable. Finally, the developed method was successfully applied for ibuprofen determination in human blood samples.

1. Introduction

Ibuprofen [2-(4-Isobutylphenyl) propionic acid] is a clinically important nonsteroidal anti-inflammatory drug (NSAID) [1]. It is used to treat mild pain even moderate such as dysmenorrhea, headaches, dental pain, postoperative pain and musculoskeletal/joint disorders including osteoarthritis, rheumatoid arthritis and ankylosing spondylitis due to its analgesic and anti-inflammatory properties [2,3]. Ibuprofen is the most widely used NSAIDs in the U.S. and Europe [4]. Its good efficacy as pain-reliever is mainly due to the phenylacetic acid moiety which mimics arachidonic acid [5].

Several analytical methods have been reported for the determination of ibuprofen in different matrices including spectrophotometry [6–10], spectrofluorimetry [11,12], conductometry [13], high-performance liquid chromatography [14–18], gas chromatography–mass spectrometry [19], infrared spectrometry [20], supercritical fluid chromatography [21], proton magnetic-resonance spectroscopy [22] and capillary electrophoresis [23–25]. However, most of these techniques are more complex and time consuming, involving the use of organic solvents or requires expensive and sophisticated instruments.

Electrochemical methods are widely investigated for the detection of ibuprofen traces. These techniques can offer a low detection limit when using efficient electrodes as noble metal electrodes [26,27], screen printed graphite electrodes [28] and chemically modified electrodes (CMEs) [29,30],

In this paper, the impregnation of the Pd–PdO particles in the sodium montmorillonite (Mt) and the oxidation of ibuprofen are applied to achieve an ultrasensitive detection of ibuprofen using differential pulse voltammetry. Sufficient reproducibility and sensitivity has been acquired using phosphate buffer (pH 8) as electrolyte solution. The experimental results showed that the oxidation parameters such as Pd–PdO/Mt amount, device settings and préconcentration time that were discussed so detailed can influence the oxidation process. The validation of the proposed method compared to HPLC as reference for ibuprofen detection was assessed. Finally, this method was successfully applied to determine trace amounts of ibuprofen in blood samples with satisfactory results.

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2. Experimental

2.1. Reagents and instruments

All chemicals used were of analytical grade. Sodium phosphate dibasic, monopotassium phosphate, sodium hydroxide, chloridric acid and palladium dichloride, were obtained from Merck, Fluka, Riedel de Haen, Chemical Companies and were used as received. Ibuprofen (IBu) drug provided by Birds Chemotec Karachi, Pakistan, was dissolved in phosphate buffer (pH 8) to prepare stock solutions of 1.0×10^{-2} mol L^{-1}. Then the working standard solutions were prepared by successive dilution by phosphate buffer. Carbon paste was supplied from Carbone, Lorraine, ref. 9900, France. The sodium montmorillonite (Cloisite-Na^{+}) with a cation exchange capacity of 92.6 cmol kg^{-1}, was obtained from Southern Clay Products, Inc.

XRD studies of prepared powder Pd–PdO/Mt were carried out using a diffractometer (XRD: Cu Kα radiation, XPERT-PRO) (kcu = 1.5406 nm) produced at 30 kVand 25 mA. The diffraction angles (2θ) were scanned between 10° and 80° with a step size of 0.02° 2θ per second.

Scanning electron microscopy (SEM) measurements were performed on an FEI Quanta 450 FEG instrument with an AMETEK energy dispersive X-ray (EDX) system (EDS SDD Bruker XFlash 5030) operated at an accelerating voltage of 30 kV.

Cyclic voltammetry, chronoamperometry and differential pulse voltammetry were carried out with a voltalab (model PST 050, Radiometer Analytical) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes; using Pd–PdO/Mt–CPE as the working, platinum plate as a counter and a system of Ag/AgCl (3.00 mol L^{-1} KCl) as the reference electrodes.

HPLC separation was investigated using a LaChrom® instrument Merck-Hitachi (Barcelona, Spain) chromatographic system equipped with a quaternary L-7100 pump and a L-7455 diode array detection system and a L-7485 programmable fluorescence detector, and a Rheodyne manual injection valve Model 7725i with 20-μL loop volume. A monolithic silica type HPLC column Chromolith® Performance RP-18e (100–4.6 mm i.d.) (VWR, Darmstadt, Germany) preceded by a guard column Chromolith® RP-18e (5–4.6 mm i.d.) (VWR, Darmstadt, Germany) was used for the separation. The collected Chromatograms with an interface module D-7000 and a personal computer were investigated by a HPLC-System-Manager HSM D-7000 (Merck-Hitachi).

2.2. Preparation of Pd–PdO/Mt-CPE

The mixture of Palladium chloride and Mt was grounded in an agate mortar. The obtained powder was calcined at different temperatures from 300 °C to 800 °C for 28 h in the kiln.

The working electrode was obtained by a mixture of carbon powder and Pd–PdO particles impregnated onto sodium montmorillonite (Pd–PdO/Mt). The resulting paste was then incorporated into the electrode cavity (laboratory made, 0.1256 cm^2 geometric surface area) and was polished by smooth paper. Electrical contact was established by a bar of carbon. The resulting electrode is hereby denoted Pd–PdO/Mt–CPE. The unmodified carbon electrode was prepared in a similar way.

2.3. Differential pulse voltammetric analysis of ibuprofen

Twenty-milliliter of supporting electrolyte were delivered in to the voltammetric cell. After recording the differential pulse voltammograms of the blank, aliquots of ibuprofen were added and the corresponding signals were recorded. A cell containing 1.0×10^{-3} mol L^{-1} of ibuprofen was utilized to investigate the influence of some chemical and electrochemical parameters in order to obtain the best analytical signal in terms of peak current (Ip). Finally, after 120 s of deposition time, the differential pulse was measured without agitation. All electrochemical measurements were performed at room temperature.

2.4. HPLC analysis of IBu

The HPLC was performed at a flow rate of 2.5 mL min^{-1}, 5 min were waited between injections, using a mobile phase constituted of 0.1% formic acid and methanol, the programmed linear elution gradient was from 40% to 70% methanol in 10 min and identification of IBu was made at 225.0 nm.

2.5. Validation of voltammetric method

2.5.1. Accuracy

To evaluate accuracy of the proposed method, the propinquity of agreement between the average value obtained from a large set of DPV results and the accepted reference value obtained using HPLC (reference method) were examined for the same solutions and then the average values, standard deviation and coefficient of variation were compared. The representative test sample consisted of a solution 1.0×10^{-6} mol L^{-1} of IBu in 1.0×10^{-1} mol L^{-1} PBS at pH = 8.0. The comparison between both methods was carried out using six portions of the same sample and each one in duplicate.

2.5.2. Linearity, limit of detection (LOD) and limit of quantification (LOQ)

Linearity range, LOD and LOQ, calibration curve (peak current values as a function of ibuprofen concentration) were verified, from which linear regression was calculated. The ibuprofen concentration was varied in the range from $1.0 \times 10-8$ mol L^{-1} to $1.0 \times 10-6$ mol L^{-1}. Each concentration was measured in triplicate.

2.5.3. Specificity

The most important goal of an analytical method is to obtain a signal free from the influence of other species contained in the sample, so this signal can be unequivocally attributed to the analyte. The selectivity of this method was investigated by analyzing four blood samples. However, the selectivity of proposed method was studied in practical application.

3. Results and discussion

3.1. Pd–PdO/Mt characterization

The X-ray diffraction patterns recorded from the raw clay and from clay-supported palladium at different temperatures for 30 h of heat treatment respectively are shown in Fig. 1A. The raw clay shows the characteristic peaks at 2θ = 6.01°, 19.56°, 21.96°, 35.48°, 45.45° and 62.17° for montmorillonite [31,32]. In addition, the number of reflection increases with increasing of the calcination temperature from 400 to 700 °C, indicating that the added catalyst has been oxidized to PdO at 2θ = 31.73°, 33.85°, 42.04°, 54.74° and 60.28° between 400 and 600 °C. Furthermore, the formation of Pd(0) was detected with a rather high temperature, at 2θ = 25.51°, 40.00°, 46.53°, 68.15° which characterize of face-centered-cubic (fcc) crystalline Pd [33].

SEM analysis was carried out to understand the topology and the size of Pd–PdO particles. Fig. 1B shows the formation of high-density, polydispersed, distorted particles of various sizes of Pd–PdO in the sodium montmorillonite, this may be the result of the heating rate, leading to the formation of rigid structure aggregates at 600 °C.

3.2. Cyclic voltammetric measurements

The voltammetric response of ibuprofen at various electrodes was recorded using cyclic voltammetry. Fig. 2a shows the cyclic voltammetric response on unmodified CPE, Mt–CPE and Pd–PdO/Mt–CPE in 1.0×10^{-1} mol L^{-1} PBS (pH 8) containing 1.0×10^{-3} mol L^{-1}