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Electrocatalytic effect of fluoroapatite in reducing paracetamol at carbon paste electrode: Analytical application

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ABSTRACT

A carbon paste electrode modified with fluoroapatite (FAP–CPE) was examined to catalyze the electrochemical reduction of paracetamol (PCT). The FAP–CPE has demonstrated an efficient performance toward PCT reduction compared to that obtained using unmodified carbon electrode. The electrochemical behavior of PCT has been investigated and the optimum experimental conditions were achieved. Moreover, a good linear relationship was achievable over the concentration range from 4.0×10^{-8} mol/L to 1.0×10^{-3} mol/L using square wave voltammetry (SWV). The detection limit (S/N = 3) was also calculated and a low value of 1.25×10^{-8} mol/L was obtained with 210 s of accumulation time. The effect of coexisting of interferent compounds such as ascorbic acid (AA), citric acid (CA) and a binary mixture with dopamine (DA) was also investigated. The proposed method was successfully applied to PCT determination in natural waters, tablets and urine samples with the results agreeing with independently verified HPLC.

1. Introduction

Drug analysis plays a major role in the quality control of drug formulations which has great health risks. A simple, sensitive and accurate method to determine the active ingredients in drugs seems essential [1].

Paracetamol (acetaminophen) is one of the important drug having antipyretic and analgesic properties most frequently prescribed throughout the world. It has been proved to be extremely efficient for the mild pain relief, muscular aches, neuralgia, migraine headache, rheumatic pain, fever and osteoarthritis [2].

In general, PCT seems to be safe and appears to have no toxic effects on human's health when taken in normal therapeutic doses [3]. However, taking high doses of PCT may cause adverse effects in the body, although in proper doses it does not display any side effects. Nowadays, PCT is widely used for its remarkable therapeutic characteristics thus precise determination and control of its quality is vital [4].

The review of literature for the assessment of PCT either individual or in combined dosage form reveals that a number of methods have been reported based on various analytical techniques. Those established methods include capillary electrophoresis (CE) [5], high performance liquid chromatography (HPLC) [6–8], HPLC-tandem mass spectrometry [9], TLC [10], UV-spectrophotometry [11,12], titrimetry [13], spectrofluorometry [14], colorimetry [15], Fourier transform infrared spectrometry [16] and thermogravimetric analysis (TGA) [17]. However, although the analysis of PCT has been extensively studied, to our knowledge few works based on electrochemical methods using modified electrodes have been developed [18–20]. In addition, the electrochemical methods are very simple, highly sensitive and low apparatus cost than other traditional methods [21]. It is noteworthy, that the modified electrodes show a high sensitivity and selectivity toward the determination of PCT [22,23] than the unmodified ones [24].

The low biodegradability of PCT motivates us to develop the redox methods favoring its electrochemical activity. Indeed, the electrocatalytic reduction or oxidation can be advantageously applied to the extensive treatment of real matrices to detect and eliminate PCT. Consequently, a suitable catalyst is of great interest in real applications and it can be used to accelerate the reduction of PCT with a significant increase of the reduction currents and a shift of potentials towards less negative values.

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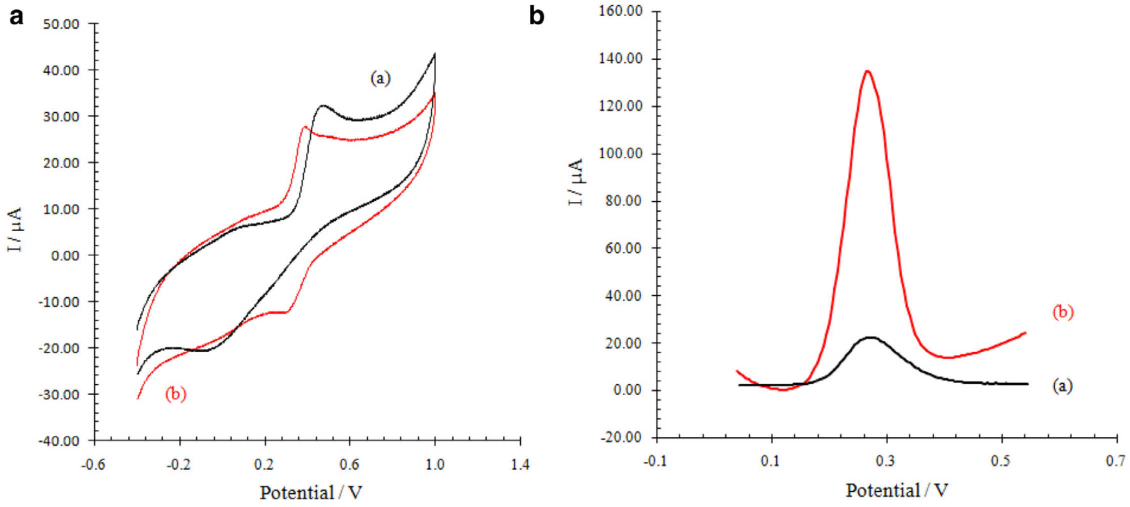

Fig. 1. (A) CVs of 1.0×10^{-4} mol/L PCT on the (a) CPE and (b) FAP–CPE at scan rate of 50 mV/s in 0.1 mol/L PBS (pH 7.0). (B) Square wave voltammograms of 1.0×10^{-4} mol/L PCT in 0.1 mol/L PBS at (a) CPE and (b) FAP–CPE (FAP/CP of (6/4: w/w).

Continuing with our interest in the use of fluoroapatite (FAP) as a carbon paste modified electrodes having sensing probes toward the oxidation or reduction of various electroactive species [25,26]. Among the different inorganic solids, FAP has advantages because it is cheap, readily available, stable in water, non-toxic, not a pollutant and, in particular, the fluorapatite is reputed unanimously for their weak solubility [27], herein we report an efficient and pertinent method for the electroreduction of PCT using square wave voltammetry. This methodology has been successfully applied to construct an enhanced sensing platform for the electrochemical detection of PCT in natural water samples, commercial tablets and human urines without any sample pre-purification steps.

2. Experimental

2.1. Reagents

All chemicals used were of analytical grade or of the highest purity available. FAP [28], sodium hydroxide, sodium phosphate dibasic, monosodium phosphate and chloridric acid were purchased from commercial sources and used as received.

Paracetamol (Malinkroute, 99.99%) was dissolved in phosphate buffer solution (0.1 mol/L) to prepare stock solutions of 1.0×10^{-3} mol/L. Then the working standard solutions were prepared by successive dilution of the stock solutions by sodium sulfate. Carbon paste was supplied from Carbone, Lorraine, ref 9900, France. All the reagents used were of analytical grade. Distilled water (DW) was used throughout the preparation of the solutions.

2.2. Instrument

Electrochemical measurements were carried out by using an eDAQ e-corder/potentiostat EA163 controlled by eDAQ EChem data acquisition software and equipped with three electrode system mounted on cell. Working electrode was FAP-modified carbon paste electrode, the counter electrode was a platinum plate and $Ag/AgCl/Cl^-$ (3 mol/L) served as reference. The pH-meter (Radiometer, sensION^{TM}, PH31, Spain) was used for adjusting pH values.

The electrochemical impedance measurements were done via an electrochemical impedance analyzer potentiostat (model PGZ 100, Eco Chemie B.V., Utrecht, The Netherlands) using a computer controlled by voltalab master 4 software logiciel.

2.3. Preparation of the chemically modified electrode

The modified carbon-paste electrode was prepared by mixing the graphite powder with the fluoroapatite to give a ratio FAP/CP of (6/4 : w/w). Portions of the resulting composite material were then packed into a home built electrode assembly consisting of the cavity (geometric area 0.1256 cm^2) of PTFE cylindrical tube electrode of a plastic pipette tip. Electrical contact was established with a bar of carbon.

2.4. Electrochemical measurements

A glass cell was washed with 10% hydrochloric acid then rinsed with DBW. Two-step procedures were followed for the analytical determination of PCT in aqueous samples. At open circuit, the working electrode was first immersed in 0.1 mol/L phosphate buffer solution (PBS) containing PCT. Where the accumulation of PCT was achieved chemically, the square wave experiments were performed in PBS electrolyte solutions at FAP–CPE. The potential range was performed from 0.0 mV to 500 mV with a frequency of 30 Hz, pulse height of 40 mV and modulation amplitude 5 mV at scan rate 150 mV/s. The cyclic voltammogram was recorded between −0.4 and −1.0 V. EIS was performed between 100 kHz and 100 mHz at AC amplitude of 10 mV. All measurements were performed at room temperature.

2.5. HPLC analysis of paracetamol

The chromatographic separation was applied using a mobile phase of water and methanol (20/80), through a Nucleosil 100-5 C18 (250 × 4.6 mm I.D. 5 µm) column (Macherey-Nagel, Germany), with an injection volume of 10 µl, and a flow rate set to 1.0 mL/min. The detector responses were measured in terms of peak area, using the Borwin chromatographic software for storage, and data mining process.

3. Results and discussion

3.1. Electrocatalytic behaviors of PCT at FAP–CPE

3.1.1. Comparisons between CPE and FAP–CPE

The electrochemical response of 1.0×10^{-4} mol/L PCT in 0.1 mol/L phosphate buffer (pH 7) at the working electrodes have been studied by using cyclic voltammetry (Fig. 1A). On the unmodified CPE (Fig. 1Aa), PCT shows a quasi-reversible redox. In the case