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Electrochemical determination of naproxen in the presence of acetaminophen using a carbon paste electrode modified with activated carbon nanoparticles

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ABSTRACT

In this study, cyclic voltammetry and differential pulse voltammetry were used to determine the electrochemical properties and concentration of naproxen in pharmaceutical formulation and human serum samples by using a carbon paste electrode modified with activated carbon nanoparticles. Optimum conditions were obtained at an electrode with 0.005 g activated carbon nanoparticles in a phosphate buffer solution of pH 6 as a supporting electrolyte. Linear calibration curves were obtained in the range of 0.1–120 μM, and the detection limit of naproxen determined was 0.0234 μM. The modified electrode shows good selectivity for naproxen in the presence of some organic and inorganic interferences and very good precision in real samples. Finally, naproxen was measured in the presence of acetaminophen.

1. Introduction

Naproxen [(+)-2-(6-methoxy-2-naphthyl)propionic acid] is an analgesic, anti-inflammatory, and antipyretic drug used in the treatment of rheumatoid arthritis, osteoarthritis, gout, nonrheumatic inflammation, and migraine. In some cases, it is also effective in reducing pain of orthopedic surgery, muscle cramps, and muscle stiffness [1]. Naproxen should be given with caution in elderly patients with kidney problems and in patients with inflammatory disease of the upper or lower channel of ear duct, hemophilia, platelet coagulation dysfunction, and gastrointestinal bleeding [1]. Different procedures have been developed for the determination of naproxen. They include capillary electrophoresis [2], spectrophotometric [3] and fluorometric determination [4–6], spectrofluorometry [7,8], second-derivative synchronous fluorescence spectroscopy [9], synchronous luminescence spectrometry [10], chemiluminescence [11,12], phosphorescence [13,14], high-performance liquid chromatography [15–19], and electrochemical techniques [20–25]. Among these methods, electrochemical techniques have received a lot of attention, as they are simple, economical, and precise. Because electrochemical measurement of pharmaceutical and biological compounds was not possible with conventional electrode because of overvoltage, electrodes were modified with nanoparticles. The nanostructure materials have different and important physical and chemical properties because of their nanoscale. Due to these features, nanomaterials can be used as a tool to develop and improve analytical processes. In this study, activated carbon nanoparticles (ACNPs) were used as a modifier. Activated carbon has a crystalline form, which is a good absorbent substance because it has a lot of pores in its internal structure [26]. This material is produced by the pyrolysis of organic materials and carbonaceous sources such as coal, peat, wood, sawdust, and nutshells, and its applications mainly depend on the raw

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material and the production process [27,28]. High internal surface area, high porosity, ability to absorb gases, and chemical liquids are unique features of activated carbon, which would render it as an excellent absorbent material used in the carbon electrode structure [29]. Therefore, using electrochemical methods by electrode modified with ACNPs, in addition to improving the surface of electrode for oxidation of drug and reducing the overvoltage, increases the sensitivity, accuracy, and selectivity of electrode. Determination of naproxen is the main aim of this study. On the basis of the conducted research, the use of a carbon paste electrode (CPE) modified with ACNPs has not been reported for the measurement of naproxen until now. Therefore, first, a modified CPE with ACNPs (ACNP/CPE) was made, and all parameters that can have effects on the current of naproxen (including instrumental and chemical parameters) were optimized; then, the naproxen in pharmaceutical and physiological samples is measured by using the prepared electrode. Measurement of naproxen in the presence of acetaminophen is another goal of this study. Therefore, finally, simultaneous measurement of acetaminophen and naproxen was done with modified electrode.

2. Experimental section

2.1. Chemicals and reagents

All of the chemical materials used in this study are listed in Table 1. As can be seen from Table 1, all reagents had analytical grades and were purchased from Merck (Darmstadt, Germany). ACNPs with an average size of 20–30 nm (Fig. 1) were purchased from Degussa Company. All solutions were freshly prepared with deionized water. Graphite powder and paraffin oil (DC350, density = 0.88 g cm^{-3}), as binding agents (both from Merck), were used for preparing the pastes. The buffer solutions were prepared from orthophosphoric acid and its salts, and its pH range was between 2.0 and 9.0.

2.2. Apparatus

In this study, an Autolab potentiostat PGSTAT 30 (Eco Chemie B.V., Netherlands) was used for electrochemical measurements including cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectroscopy (EIS), which contains a cell with three electrodes in the sample solution. These three electrodes are modified or unmodified CPE as working electrode, Ag/AgCl (3.0 M KCl) as reference electrode, and platinum wire as counter electrode. EIS experiments were obtained in the Fe^{2+}/Fe^{3+} solution (0.1 M KCl solution containing 10 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$), as the redox probe, at the open-circuit potential and over the frequency range of 0.01 Hz–100 kHz. Phosphate buffers with various pH values were made using Metrohome 827 pH meter. Analytical digital scale Skaltek SBA31 (d = 0.0001 g) was used to weigh chemicals, and Excel software was used to record the voltammogram curves and calculations.

Table 1
List of chemical materials used in this study.

Chemical	Chemical formula	Purity (%)	Company
Acetic acid	$C_2H_4O_2$	100	Merck
Phosphoric acid	H_3PO_4	85	Merck
Sodium dihydrogen phosphate	NaH_2PO_4	99	Merck
Disodium hydrogen phosphate	Na_2HPO_4	99	Merck
Boric acid	H_3BO_3	99	Merck
Sodium hydroxide	NaOH	99	Merck
Naproxen	$CH_3OC_{10}H_4CH(CH_3)CO_2H$	99	Merck
Paraffin oil		100	Merck
Graphite powder	C	100	Merck
ACNPs	C	99	Degussa

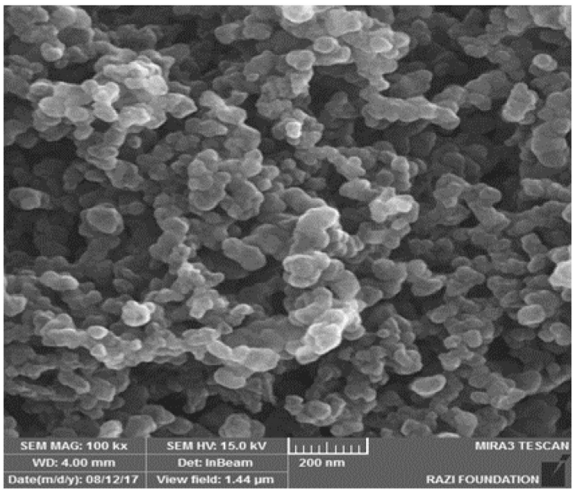

Fig. 1. Scanning electron microscopy image of ACNPs.

2.3. CPE preparation

CPE, formed from the mixture of graphite powder with nonconductive organic compounds and insoluble materials in water, has a renewable surface, low price, and low current field. The composition of carbon paste is highly effective in electrode activity. For modification of carbon paste with ACNPs, first, 0.5 g of graphite powder was grinded in an agate mortar for 20 min. Then, 0.005 g of ACNPs were added to the graphite powder and after grinding for 20 min, about seven to eight drops of paraffin oil were added to it. The obtained homogeneous paste was compacted into an insulin syringe with a cross-section of 1.34 mm, and to connect the electrical device and drug solution in electrochemical measurements, a copper wire was imported into the carbon paste from the end of the syringe and was prepared to work with the electrochemical device.

3. Results and discussion

3.1. Definition of the appropriate amount of ACNPs for modification of electrode

Because ACNPs can affect the response of the electrode relative to naproxen, its amount was changed from 0.001 to −0.007 g, and CV and DPV of buffer solution, containing 10 μM of naproxen, were recorded. The results illustrated