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Development and application of an electrochemical sensor modified with multi-walled carbon nanotubes and graphene oxide for the sensitive and selective detection of tetracycline

Ademar Wong [a,*], Mateus Scontri [a], Elsa Maria Materon [a], Marcos R.V. Lanza [b], Maria D.P.T. Sotomayor [a]

[a] Department of Analytical Chemistry, Institute of Chemistry, State University of São Paulo (UNESP), 14801-970 Araraquara, SP, Brazil
[b] Instituto de Química de São Carlos, Universidade de São Paulo, P.O. Box 780, CEP 13560-970 São Carlos, SP, Brazil

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ABSTRACT

In this work, an electrochemical sensor based on a carbon paste electrode modified with a combination of multi-walled carbon nanotubes functionalized with carboxyl groups (MWCNT-COOH), together with graphene oxide (GO), was developed for the sensitive and selective determination of tetracycline. Electrochemical sensors were constructed using carbon paste modified with 2.6% (*w*/*w*) of MWCNT-COOH and 3.1% (*w*/*w*) of GO. Under the optimal conditions using adsorptive stripping differential pulse voltammetry (AdSDPV), the sensor showed a linear response for tetracycline concentrations between 2.0×10^{-5} and 3.1×10^{-4} mol L^{-1}, sensitivity of 1.2×10^4 μA L mol^{-1}, and a detection limit of 3.6×10^{-7} mol L^{-1}. The incorporation of GO and MWCNT-COOH in the carbon paste improved the sensitivity, selectivity, and stability of the device. The MWCNT-COOH-GO/CPE sensor was successfully applied for the detection of tetracycline in river water, artificial urine, and pharmaceutical samples, without any need for sample pretreatment. The relative standard deviation (RSD) of the electrochemical measurements was less than 6.0% (n = 3).

1. Introduction

Tetracycline is one of the antibiotics most commonly used to treat bacterial diseases such as urinary tract infections, chlamydia, and acne. The extensive use of this drug in veterinary medicine has led to its accumulation in food products including meat, milk, honey, and chicken [1]. The impacts of exposure to low levels of antibiotics such as tetracycline include the development of antibiotic-resistant genes, vision problems, teeth discoloration, and allergic symptoms in humans [2,3]. Considering these concerns, it is important to develop analytical methods for the determination of low levels of tetracycline in the environment. Many analytical methods have been reported for tetracycline, such as HPLC [4], spectrophotometry [5], capillary electrophoresis [6], chemiluminescence [7], and electrochemical approaches [8]. With the exception of the electrochemical methods, these techniques require relatively expensive instrumentation, have long times of analysis, and require trained personnel.

Electrochemical sensors and biosensors are widely used in the monitoring of different substances. Carbon, platinum, gold, and silver electrodes are most common, offering the advantages of a wide potential window, low background current, chemical inertness, and low cost [9–11]. The modification of these electrodes with suitable nanostructured materials is fundamental for achieving faster electron transfer between the electrode and the analyte, a low detection limit, a wide linear response range, good stability and reproducibility, and increased sensitivity and selectivity of the electrochemical sensor [12–16]. The nanostructured materials studied in this work were multi-walled carbon nanotubes and graphene oxide.

Carbon nanotubes have attracted much attention due to their advantageous mechanical, optical, chemical, and electrical properties. Various applications of carbon nanotubes have been investigated, including their uses in field emitters, quantum wires, batteries, optoelectronic components, ultra-strength engineering fibers, and nanoelectronic devices [17–21]. Recent studies have demonstrated that modification of an electrode with carbon nanotubes can promote high electrocatalytic activity for the detection of captopril, vitamin C, hydrogen peroxide, and some important catecholamine substances such as dopamine, epinephrine, and cytochrome c, among others [18,21–23].

Graphene oxide (GO), a nanomaterial with sp^2 hybridization, has extraordinary electrical, physical, and chemical properties. Nanomaterials composed of GO have high surface areas, high specific capacitance, and exhibit electronic transport properties. These features make them attractive for use in energy conversion, field-effect transistors, and batteries. Their applications in electronic device include electrochemical sensors and biosensors for the sensitive determination of analytes including nitrogenous bases (adenine and guanine), pesticides (such as carbofuran), drugs (ascorbic acid, dopamine, and uric acid), diethylstilbestrol, and others [24–28]. Derived from graphene, GO is formed in

* Corresponding author.
E-mail address: ademar.wong@hotmail.com (A. Wong).

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individual layered sheets that contain abundant C–O–C (epoxide), C–OH, and COOH functional groups located in the basal planes and at the edges [29,30]. Since they have similar compositions, GO and carbon nanotubes exhibit similar physical and chemical properties.

The aim of this work was to develop a sensitive, selective, and stable electrochemical sensor for the determination of tetracycline in pharmaceutical, river water, and artificial urine samples. For this purpose, the working electrode was modified with GO and MWCNT-COOH, and the experimental conditions were optimized in order to maximize the performance of the sensor.

2. Materials and methods

2.1. Reagents and solutions

The reagents used in this work were either analytical or HPLC grade. All aqueous solutions were prepared with deionized water (18 MΩ cm at 25 °C) obtained from a Milli-Q Direct-0.3 (Millipore) purification system. MWCNT, graphene, mineral oil (Nujol), and graphite powder (<20 μm) were acquired from Sigma-Aldrich. NaOH, $NaH_2PO_4.H_2O$, TRIS, and PIPES were obtained from Synth (Brazil).

A stock solution of 8.0×10^{-3} mol L^{-1} tetracycline was prepared by dissolving 0.04 g of the compound in 10.0 mL of deionized water. The mixture was sonicated for 1 min to ensure complete dissolution of the tetracycline.

2.2. Electrochemical measurements

All voltammetric measurements were performed using a potentiostat (Model μ-Autolab Type III, Autolab/Eco Chemie) fitted with an electrochemical cell containing three electrodes: a commercial Ag/AgCl(KCl_{sat}) reference electrode (Analion), a platinum wire as the counter electrode, and a modified carbon paste electrode as the working electrode (r = 1.2 mm).

2.3. Construction of the electrochemical sensor

2.3.1. Preparation of the modified carbon paste electrode

The carbon paste electrode (CPE) was prepared using a mixture of 89 mg of graphite powder, 5 mg of MWCNT-COOH, 6 mg of GO, and 1 mL of 0.1 mol L^{-1} phosphate buffer solution (pH 7.0). Phosphate buffer was used to improve the conductivity of the carbon paste. The material was carefully homogenized for 20 min using a mortar and pestle, and then left to dry at room temperature. Afterwards, 85 μL (90 mg) of mineral oil was added to obtain a paste. The paste was then packed into the cavity of the Teflon working electrode (4 mm i.d., 1 mm depth), where a Pt disk was used to provide the electrical contact. The

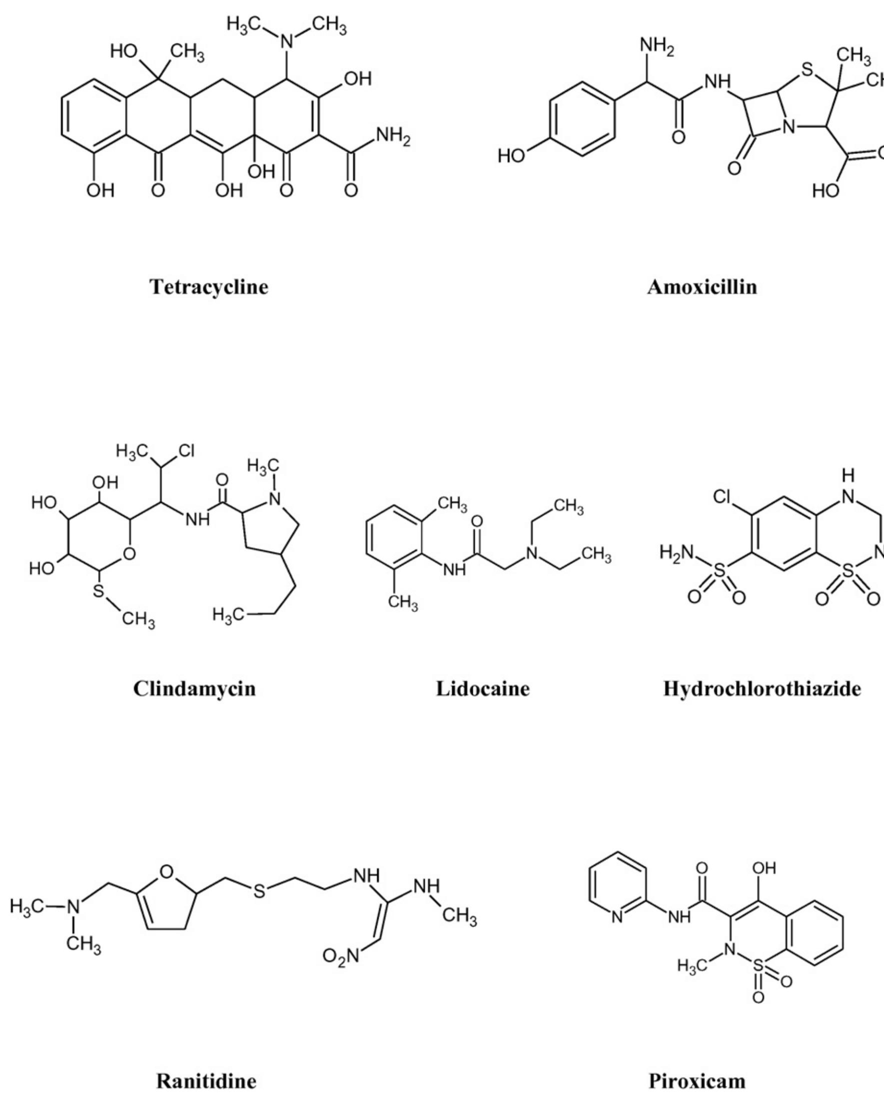

Chart 1. Chemical structures of pharmaceutical formulations analyzed in the study of selectivity.