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Electroanalysis of formetanate hydrochloride by a cobalt phthalocyanine functionalized multiwalled carbon nanotubes modified electrode: characterization and application in fruits

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ABSTRACT

This study characterizes the electroanalytical behavior of the carbamate pesticide formetanate hydrochloride (FMT) at a cobalt phthalocyanine (CoPc) functionalized multiwalled carbon nanotubes (*f*MWCNT) modified glassy carbon electrode (CoPc-*f*MWCNT/GCE). Nafion® was used to improve solubility and dispersibility of *f*MWCNT. The construction of the developed electrode was characterized by high-resolution field-emission gun scanning electron microscopy, Raman spectroscopy, cyclic voltammetry and electrochemical impedance spectroscopy. FMT exhibited a behavior consistent with a three-step reaction of the electrochemical-chemical-electrochemical mechanistic type at CoPc-*f*MWCNT/GCE (three anodic peaks at 0.26, 0.55 and 1.2 V, and two cathodic peaks at 0.35 and 0.50 V *vs.* Ag/AgCl/3 M KCl). Highly reproducible and well-defined peaks were obtained at the optimum experimental conditions (Britton-Robinson buffer at pH 5.0, accumulation potential 1.55 V, accumulation time 5 s, frequency 100 s^{-1}, amplitude 30 mV, and scan increment 3 mV). Peak currents were found to be proportional to the FMT concentrations in the range of 9.80×10^{-8} to 3.92×10^{-6} mol dm^{-3} with a detection limit (LOD) of 9.7×10^{-8} mol dm^{-3}. The modification of GCE with CoPc-*f*MWCNT enhanced the electrocatalytic activity and provided high sensitivity (3.51 A mol^{-1} dm^3). The developed electroanalytical methodology was successfully applied to FMT residue analysis in mango and grape samples with recoveries in the range of 94.2 ± 4.5 to 105.7 ± 1.8%. The proposed electroanalytical approach represents a reliable, sensitive and environmental friendly analytical alternative for determination of FMT.

1. Introduction

Current concerns of the deleterious environmental and health impacts of carbamate pesticides have been increasing. Humans and other non-target species are exposed to residues of these cholinesterase-inhibiting chemicals via nutritional sources (legumes, fruits, contaminated meat, dairy products, *etc.*), water and/or through environmental/occupational settings [1]. As a member of the N-methyl carbamate class of chemicals, formetanate hydrochloride (3-dimethylaminomethyleneaminophenyl methylcarbamate hydrochloride; FMT) shares the common mechanism of toxicity. It is a miticide/insecticide registered for use on several fruits (grapefruit, lemon, lime, nectarine, orange, tangelo, tangerine, *etc.*) and nonagricultural uncultivated areas/soils [2]. In this context, the development of electrochemical devices is a key tool for implementation of rapid, sensitive, versatile, environmental friendly, *in situ* real-time and cost-effective residues screening programs [3]. Moreover, electrochemical sensors can also provide information regarding kinetic and mechanistic aspects of degradation [4–6].

Nanostructured carbon materials have proved to be very interesting in various research fields due to their inherent advantages such as excellent electrical conductivity, high-surface to volume ratio, significant mechanical strength, good chemical stability and pore structure [7–11]. The use of Nafion® to improve solubility and dispersibility of multiwalled carbon nanotubes

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(MWCNT) has provided a useful avenue for preparing MWCNT-based sensors [12]. In addition, MWCNT decorated with transition metal phthalocyanine complexes (MPc) hold great promise for designing new sensing platforms [13–17]. Phthalocyanine are 18 π-conjugated aromatic macrocycles that present remarkable optical and electrical properties, structural versatility and exceptional stability. Metal atoms (*e.g.* Co, Fe, Ni, and Cu) can be incorporated in the central region of the macrocycle to tailor some of their chemico-physical properties [18,19]. In particular, CoPc have the ability of undergoing fast redox processes, with minimal reorganizational energies, and can act as electron transfer mediator for several compounds. The immobilization of CoPc on suitable substrates can lead to modified electrodes with electrocatalytic properties [20]. In biosensor design, such as cholinesterase modified electrodes, CoPc were indicated as one of the most suitable for the detection of thiol-containing molecules [21], and has been used as electronic mediator to decrease the applied potential (from *ca.* 410 to 100 mV *vs.* Ag/AgCl), hindering the oxidation of other compounds thus reducing the interferences [22]. Enzymes were successfully immobilized on CoPc modified electrodes by entrapment in a photocrosslinkable polymer (PVA-AWP) [23,24]. Scarce studies have demonstrated the potential of MPc-MWCNT systems to improve the sensitivity of modified electrodes for pesticides (asulam, carbaryl, glyphosate and metolcarb) analysis [11,25–28] mostly in (tap/natural) waters and synthetic aqueous solutions [11,25–27]. Novel electrocatalytic platforms based on CoPc integrated with MWCNT for electroanalysis of pesticides in food commodities need clearly to be further explored. No electrochemical method based on MPc-MWCNT modified electrode for FMT detection was found in the literature so far, nor any mechanistic proposal involving its oxidation and reduction. FMT electroanalysis was only reported in four works [29–32]. FMT reduction was characterized at the dropping mercury electrode [29]. More recently, FMT was indirectly quantified by three different enzymatic biosensors [30–32]. However, the developed biosensors presented limited specificity since other pesticides from the carbamates family may also inhibit the enzymatic catalysis. Also, modified electrodes with biological components are more difficult to work with and less robust (to pH, temperature, applied potential, storage, etc.) [26].

Therefore, the main aims of this work were: i) to explore the advantages of combining CoPc and functionalized MWCNT solubilized in Nafion® (*f*MWCNT) for modification of glassy carbon electrode (GCE), ii) to develop and optimize a rapid, simple, accurate and low-cost sensitive electrochemical approach for FMT analysis based on the modified electrode (CoPc-*f*MWCNT/GCE), and iii) to propose a mechanism for the electrochemical behavior of FMT. The preparation of CoPc-*f*MWCNT/GCE was fully characterized by high resolution field-emission gun scanning electron microscopy (FEG-SEM), Raman spectroscopy, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Considering that real sample applications of electrochemical devices are rare, the performance of CoPc-*f*MWCNT/GCE for FMT quantification in fruits was also assessed. The chosen fruit species are those that have the lowest (0.02 mg kg^{-1} in mango) and the highest (1.0 mg kg^{-1} in grapes) established Brazilian FMT maximum residue limits (MRLs) [33].

2. Experimental

2.1. Reagents

Formetanate hydrochloride (certified purity higher than 99.6%), CoPc (97% purity), Nafion® (10 wt. % in H_2O) and pristine MWCNT (O.D. × L 6–9 nm × 5 μm, >95%) were purchased from Sigma–Aldrich (Steinheim, Germany). Standard solutions of FMT were prepared daily by dissolving an accurately weighed amount in ultrapure water. Britton-Robinson buffer (BR, 0.04 mol dm^{-3}) was prepared by mixing 0.04 mol dm^{-3} of phosphoric, acetic and boric acid. All other chemicals were of analytical grade. The ultrapure water (18.2 MΩ cm) was produced by a Milli-Q system (Millipore, Molsheim, France).

2.2. Electrode pretreatment and modification

Firstly, the functionalization of 500 mg of pristine MWCNT was carried in a 250 mL mixture of H_2SO_4:HNO_3 (3:1; v/v) with magnetic stirring at 26 ± 1 °C for 4 h [34–36]. The *f*MWCNT were filtered through a 0.45 mm Nylon filter membrane (Millipore, Molsheim, France), washed with ultrapure water, and dried in oven at 70 °C for 12 h [26,34–36].

Prior to the modification, the GCE (geometric area of 0.0314 cm^2 Metrohm, The Netherlands) was polished with 3.0 μm diamond paste slurry, rinsed with ultrapure water, cleaned ultrasonically in acetone and water alternatively for 3 min, and then dried with nitrogen. 1 mg of *f*MWCNT plus 1 mg of CoPc were dispersed by ultrasonic stirring for 30 min in 1 mL of dimethylformamide (DMF) containing 0.5% Nafion® (DMF/Nafion® 0.5%). Next, 0.5 μL of the CoPc-*f*MWCNT suspension was dropped on the cleaned GCE surface, and dried at 26 ± 1 °C for 1 h. The other tested electrodes, i.e., 0.5% Nafion®/GCE (modified with DMF/Nafion® 0.5%), MWCNT/GCE (modified with MWCNT dispersed in DMF/Nafion® 0.5%) and *f*MWCNT/GCE (modified with functionalized MWCNT dispersed in DMF/Nafion® 0.5%) were prepared similarly.

Surface characterization of the modified GCE was accomplished by FEG-SEM using a FEG-Zeiss model Supra 35-VP (Carl Zeiss, Germany). Raman spectroscopy assays of the several tested modifications (MWCNT, *f*MWCNT and CoPc–*f*MWCNT prepared as described above) were carried out on a Horiba Jobin Yvon model HR550 spectrometer using the 514.5 nm excitation line from an argon ion laser ion.

2.3. Electrochemical studies

Electrochemical experiments were performed with a potentiostat/galvanostat, AUTOLAB model PGSTAT 30 (Metrohm-Eco Chemie, The Netherlands) controlled by a computer through the Model NOVA version 1.9 software. A conventional electrochemical cell consisting of an Ag/AgCl/3 M KCl reference electrode, a platinum plate as the auxiliary electrode, and 0.5% Nafion®/GCE, MWCNT/GCE, *f*MWCNT/GCE, CoPc-*f*MWCNT/GCE as working electrode were used. CV and square wave-voltammetry (SWV) experiments were carried out in 0.04 mol dm^{-3} BR buffer (pH 5.0) over the potential range of 0.0 to 0.8 V or 0.0 to 1.5 V. The optimal SWV parameters were: accumulation potential (E_{acc}) 1.55 V, accumulation time (t_{acc}) 5 s, frequency (*f*) 100 s^{-1}, amplitude (*a*) 30 mV and scan increment (ΔE_s) 3 mV. EIS assays were performed in the presence of 1.0×10^{-3} mol dm^{-3} $Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$(1:1) in 0.1 mol dm^{-3} KCl at a frequency range of 10^{-1} to 6×10^4 s^{-1} and amplitude perturbation 5 mV. All measurements were carried out, at least, in triplicate.

2.4. Application to fruits

Fruit samples were acquired from local supermarkets at Fortaleza (Brazil). Samples of mango and grape were taken, chopped and homogenized in accordance with the guidelines of the European Council Directive [37]. Pesticide extraction was performed by the Quick, Easy, Cheap, Effective, Rugged and Safe – QuEChERS method [31,38,39]. An aliquot of 15 g of homogenized sample was quantitatively transferred to a QuEChERS tube containing the buffer–salt mixture 6 g magnesium