



Enhanced host–guest electrochemical recognition of herbicide MCPA using a β -cyclodextrin carbon nanotube sensor

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ABSTRACT

An electrochemical sensor for the determination of the chlorophenoxy herbicide MCPA has been developed, based on a combination of multi-walled carbon nanotubes with incorporated β -cyclodextrin and a polyaniline film modified glassy carbon electrode. The proposed molecular host–guest recognition based sensor has a high electrochemical sensitivity for the determination of MCPA. The electrochemical behaviour of MCPA at the chemically modified electrode was investigated in detail by cyclic voltammetry. The results indicate that the β -CD/MWCNT modified glassy carbon electrode exhibits efficient electrocatalytic oxidation of MCPA with high sensitivity, stability and lifetime. The analytical characteristics of this film were used for the quantitative determination of MCPA in natural waters. Cyclic voltammetry in phosphate buffer solution at pH 6.0, allowed the development of a method to determine MCPA, without any previous steps of extraction, clean-up, or derivatization, in the range of 10–100 $\mu\text{mol L}^{-1}$, with a detection limit of 0.99 $\mu\text{mol L}^{-1}$ in water. The results were statistically compared with those obtained through an established high-performance liquid chromatography technique, no significant differences having been found between the two methods.

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1. Introduction

Agricultural and industrial chemicals, pollutants and toxicants are now widely dispersed in the environment. Among them, pesticides are used extensively in agriculture and industry to enhance food production by eradicating unwanted insects and controlling disease vectors [1,2]. The presence of pesticide residues and metabolites in food, water and soil currently represents one of the major issues for environmental chemistry. In fact, these chemicals are known to have a cumulative hazardous effect on humans and animals; thus, regulations for drinking water are required in order to limit human risks and environmental pollution [3].

Phenoxy acid herbicides showing auxin-like activity have been extensively used to control the growth of grass and broad-leaf weeds in many crops, such as rice [4], winter wheat [5,6], soybean [7], etc. The chlorophenoxy herbicide MCPA (4-chloro-2-methylphenoxyacetic acid) is widely used for the control of broad-leaf weeds primarily in cereal and grass seed crops [8–10]. In Portugal,

MCPA still remains one of the most often-used herbicides for rice crops [11]. MCPA is not extensively metabolised and urine is the predominant route of excretion [12]. Although MCPA is only a moderately toxic herbicide, monitoring its residues in water and soil is crucial because it can influence the nervous system upon adsorption through the skin and its prolonged inhalation can cause dizziness, burning in the chest and coughing [13].

Contemporary methods for environmental determination and/or the monitoring of pesticides include gas and liquid chromatography and various spectroscopic techniques [14]. Each of these approaches suffers from several disadvantages such as being costly, time-consuming, not sufficiently sensitive and/or requiring complex sample preparation. Moreover, continuous monitoring is not possible with any of these methods and it follows that a simplified analytical approach would prove highly beneficial.

A potential solution to this problem is the utilisation of electrochemical sensor technology. Electrochemical sensors can provide fast, reliable and cost-effective measurement and monitoring methods. The new demands of environmental analysis have driven the development of more selective and sensitive sensing systems and the advent of nanotechnology has led to great advances in detection strategies. Attractive properties of nanomaterials such as large surface to volume ratio, high packing density and long-range order may serve to be potentially useful in emerging environmental applications. Carbon nanotubes (CNTs)

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have generated great interest in applications based on their field emission and electronic transport properties, their high mechanical strength, high-surface to volume ratio and their chemical properties [15]. The combination of CNT electrocatalytic activity with the known advantages of other compounds, such as polymers, enzymes or macromolecules, can be a very important and new way for solving electroanalytical challenges.

The molecule β -cyclodextrin (β -CD), a macrocyclic compound with seven D-glucopyranose units linked by α -1,4-glycosidic bonds which possesses a hydrophilic exterior and an interior hydrophobic cavity, has been extensively investigated in host-guest chemistry for the construction of versatile supramolecular aggregations owing to its special hydrophobic cavities and ability to improve the physico-chemical properties and chemical stability of drugs [16–18]. Electroanalytical applications of CDs are based on formation of an inclusion complex, molecular recognition and selective pre-concentration of analytes at the electrode [19].

Taking into consideration the electrochemical properties of CNTs as well as the reported properties of CD, this work proposes a novel strategy based on the simultaneous modification of a glassy carbon electrode with a novel polyaniline-CNT cyclodextrin matrix (PANI- β -CD/MWCNT) for the determination of MCPA herbicide. The chemical recognition of MCPA by the use of CD is combined with the added advantage of a faster electron transfer process due to the CNT present at the electrode interface. The modified electrode developed was employed for the direct oxidative determination of MCPA in pure and natural water samples by cyclic voltammetry.

2. Experimental

2.1. Reagents

Multi-walled carbon nanotubes (MWCNTs) were obtained from NanoLab (USA). MCPA, aniline and β -cyclodextrin (β -CD) were supplied by Sigma-Aldrich Química (Sintra, Portugal). Analytical grade reagents purchased from Merck (Darmstadt, Germany) were used without additional purification.

Double distilled deionized water was used throughout the experiments. Buffer solutions employed for voltammetric determinations were 0.1 M in the pH range 1.2–12.2.

HPLC-grade acetonitrile was obtained from Carlo Erba. Prior to use, the solvents were filtered through a 0.45- μ m filter.

2.2. Apparatus

Voltammetric experiments were performed using an Autolab PGSTAT 12 potentiostat/galvanostat (EcoChemie, Netherlands) in a one-compartment glass electrochemical cell equipped with a three-electrode system consisting of a bare or modified glassy carbon working electrode (GCE, $d=2$ mm), a platinum wire counter electrode and an Ag/AgCl (saturated KCl) reference electrode. All measurements were carried out at room temperature.

A Crison pH-meter with glass electrode was used for the pH measurements (Crison, Spain).

The HPLC method [20] was performed using a HPLC/DAD system consisting in a Shimadzu instrument (pumps model LC-20AD, Tokyo, Japan), equipped with a commercially prepacked Nucleosil 100–5 C18, analytical column (250 mm \times 4.6 mm, 5 μ m, Macherey-Nagel, Duren, Germany) and UV detection (SPD-M20A) at the wavelength maximum determined by analysis of the UV spectrum (234 nm). The mobile phase consisted of 43.7 mM acetic acid at pH 2.5 with 40% (v/v) acetonitrile. It was delivered isocratically at 1 mL min⁻¹ at room temperature.

The chromatographic data was processed in a Samsung computer, fitted with LabSolutions software (Shimadzu, Japan).

2.3. Preparation of modified electrochemical sensors

Multi-walled carbon nanotubes (MWCNTs) were purified and functionalised as described elsewhere [21]. A mass of 120 mg of MWCNTs was stirred in 10 mL of a 5 mol L⁻¹ nitric acid solution for 20 h. The solid product was collected on a filter paper and washed several times with double-distilled water until the filtrate solution became neutral (pH \approx 7). The functionalised MWCNTs (fMWCNT) obtained were then dried in an oven at 80 °C for 24 h. Nitric acid usually causes the significant destruction of carbon nanotubes and introduces –COOH groups at the ends or at the sidewall defects of the nanotube structure.

Two milligrams of MWCNTs or fMWCNTs was dispersed by using ultrasonic agitation in 1 mL aqueous β -CD solution (2%) to give a 2 mg mL⁻¹ black suspension.

Prior to use, the 2 mm GC working electrode was carefully polished with an aqueous slurry of alumina powder (BDH) on a microcloth pad and then thoroughly washed with double-distilled water. The electrode was then placed first in ethanol followed by double-distilled water, in each case being subjected to sonication to remove traces of alumina and possible contaminants. The clean GCE was then immersed in a solution containing 0.011 mol L⁻¹ aniline and 0.025 mol L⁻¹ H₂SO₄ and the potential was swept between –0.1 and 1.0 V vs. Ag/AgCl at a scan rate of 50 mV s⁻¹ for 50 cycles. After preparation of the polyaniline film on the GC electrode surface, an aliquot of 6 μ L of the 2 mg mL⁻¹ of the previously-prepared suspension of MWCNTs or fMWCNTs was dropped onto the electrode surface and dried in air at room temperature.

2.4. Analytical procedure

The PANI- β -CD/fMWCNT film coated GC sensor was first activated in phosphate buffer (pH 6) by cyclic voltammetric sweeps between 0.5 and 1.3 V until stable cyclic voltammograms were obtained. Accurate volumes of the stock standard solution of MCPA (10 mM) were then added to the voltammetric cell and CVs were recorded from 0.5 to 1.3 V at a scan rate of 50 mV s⁻¹. The same procedure was applied for the analysis of natural water samples. After every measurement, the PANI- β -CD/fMWCNT film coated GC sensor was cleaned by successive cyclic voltammetric sweeps in 0.1 M phosphate buffer (pH 6) solution until unchanged cyclic voltammograms were obtained.

2.5. Sample preparation

A water sample from Leça river (a polluted river with a high content of organic components) was collected in 2.5-L brown glass bottles. Immediately after arrival in the laboratory, the samples were filtered through 1- μ m glass fibre filters and 0.45- μ m cellulose acetate filters, sequentially, to remove suspended particles.

2.6. Analysis of MCPA in water samples

Standard stock solutions of MCPA (10 mM) were prepared in ethanol. For calibration curves, standard solutions were prepared in the voltammetric cell by adding accurate volumes of the stock standard solution of MCPA to the selected phosphate pH 6 supporting electrolyte in order to obtain concentrations between 10 and 100 μ M. The calibration curve for CV analysis was constructed by plotting the peak current against the MCPA concentration (10, 40, 60, 80 and 100 μ M). The limit of quantification (LOQ) and the limit of detection (LOD) were calculated according to IUPAC recommendations [22], using an S/N ratio of ten and three, respectively. Method precision was checked on different days, within day ($n=5$) and between days ($n=5$) for three different concentrations. The accuracy of the proposed method

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