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RESEARCH ARTICLE

Electrochemical sensor for simultaneous determination of herbicide MCPA and its metabolite 4-chloro-2-methylphenol. Application to photodegradation environmental monitoring

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Abstract The development and application of a polyaniline/carbon nanotube (CNT) cyclodextrin matrix (PANI-β-CD/MWCNT)-based electrochemical sensor for the quantitative determination of the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA) and its main transformation product 4-chloro-2-methylphenol in natural waters are described. A simple cyclic voltammetry-based electrochemical methodology, in phosphate buffer solution at pH 6.0, was used to develop a method to determine both MCPA and 4-chloro-2-methylphenol, without any previous extraction or derivatization steps. A linear concentration range (10 to 50 μmol L^{-1}) and detection limits of 1.1 and 1.9 μmol L^{-1}, respectively, were achieved using optimized cyclic voltammetric parameters. The proposed method was successfully applied to the determination of MCPA and 4-chloro-2-methylphenol in natural water samples with satisfactory recoveries (94 to 107 %) and in good agreement with the results obtained by an established high-performance liquid chromatography technique, no significant differences being found between the methods. Interferences from ionic species and other herbicides used for broad-leaf weed control were shown to be small. The newly developed methodology was also successfully applied to MCPA photodegradation environmental studies.

Keywords Herbicides · MCPA · 4-Chloro-2-methylphenol · Voltammetric sensor · Carbon nanotubes

Introduction

Utilization of pesticides has been, and will continue for many years to be, an important means to protect agricultural products. Many of these compounds are released to the environment either via agricultural application or as a result of accidental spills or mishandling. Pesticides entering the soil and water are subject to both abiotic and biotic transformations. Naturally occurring chemical transformations in the field include hydrolysis, redox reactions, and other reactions such as photolysis (Triegel and Guo 1994; Barceló and Hennion 1997). When pesticides degrade in the environment, they may form persistent and toxic transformation products (TPs), which should be accounted for in the environmental risk assessment of the parent compounds (Belfroid et al. 1998). TPs cannot be assessed separately from their parent compounds since they often exhibit the same mode of toxic action, and there could even be synergistic mixture effects that enhance overall toxicity (Barceló and Hennion 1997; Belfroid et al. 1998; Escher and Fenner 2011). Consequently, there is increased concern regarding the formation of TPs and their presence in the environment. This concern has been expressed in the European Regulation (EC) No. 1107/2009, which establishes the need to demonstrate potentially harmful effects of relevant metabolites on human or animal health or on groundwater, as well as methods for the analysis of residues of these compounds in plant, animal and environmental matrices and drinking water (Regulation (EC) No. 1107/2009). Therefore, there is an urgent need for fast screening techniques

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which can detect TPs in field-collected samples or in samples obtained from laboratory experiments performed under conditions that simulate real, natural environmental situations.

Phenoxyacetic herbicides are used worldwide on a large scale as plant growth regulators for agricultural purposes. Due to their solubility in water, they can move in agricultural ecosystems, causing the pollution of surface and ground waters (Cserháti and Forgács 1998). Phenoxyacetic herbicides have potential toxicity towards humans and animals and are considered as moderately toxic (class II or III) by the World Health Organization. Among the phenoxyacetic herbicides, 4-chloro-2-methylphenoxyacetic acid (MCPA) is one of the most widely used pesticides for the control of broad-leaf weeds, primarily in cereal and grass seed crops (Eurostat 2007). Environmental degradation or removal of MCPA is mainly achieved by photodegradation (Topalov et al. 2001; Bojanowska-Czajka et al. 2006). The main intermediate that is produced upon direct photolysis of MCPA is 4-chloro-2-methylphenol (Zertal et al. 2001; Costa et al. 2013). This transformation product has been detected in the Rhône delta waters, where MCPA is extensively used as a post-emergent herbicide in flooded rice farming, in concentration levels comparable to those of the parent herbicide. Laboratory studies showed that the intermediates of MCPA direct photolysis are more toxic to aquatic organisms than the parent compound (Bojanowska-Czajka et al. 2006; Zertal et al. 2001).

Considerable effort has been made to develop sensor platforms to monitor chemical xenobiotics in environmental applications. A number of electrochemical-based sensor platforms have been developed for the detection of the phenoxyacetic herbicides, namely immunoassay and screen printed-based sensors (Suri et al. 2009; Tomassetti et al. 2012; Verma and Dhillon 2003; Yang et al. 2013). The simultaneous determination of MCPA and 4-chloro-2-methylphenol in environmental samples has been proposed using analytical methods based on gas or liquid chromatography (Henriksen et al. 2001; Pozo et al. 2001; Jankowska et al. 2004). Each of these approaches suffers from disadvantages such as being costly, time-consuming and/or requiring complex sample preparation. A potential solution to this problem is the utilization of electrochemical sensor devices since they can provide fast, reliable and cost-effective measurement and monitoring. Nowadays, carbon nanotubes (CNTs) are among the most promising nanomaterials used in electrochemical sensors. Their high thermal conductivity, remarkable mechanical properties, chemical stability and high surface to volume ratio are very appealing for sensing applications (Mazloum-Ardakani and Sheikh-Mohseni 2011). The combination of CNT electrocatalytic activity with the known advantages of other modifiers, such as polymers or macromolecules, has proved to be a successful approach for solving electroanalytical challenges. Polyaniline (PANI) has attracted a great interest for technological application in chemical sensors, due to its excellent thermal and environmental stability. As one of the most promising conducting polymers, PANI has received great attention owing to its good redox reversibility, high capacitance, easy processing, stability in aqueous solution and unique proton doping/dedoping mechanism, especially with CNT (Gajendran and Saraswathi 2008; Sapurina and Shishov 2012).

Electrodes modified with multi-walled CNTs (MWCNT) in which β-CD, a macrocyclic compound that has a toroidal form with a hydrophilic exterior and a hydrophobic inner cavity, have recently been successfully used to study and quantify many biological and other organic molecules because of the promising properties of both materials (Wang et al. 2006; Shen and Wang 2009; Rahemi et al. 2012, 2013).

In this work, we report 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 simultaneous determination of MCPA herbicide and its main transformation product 4-chloro-2-methylphenol (Scheme 1). The modified electrode developed was employed for the determination of MCPA and 4-chloro-2-methylphenol in natural water samples and for following photodegradation in laboratory experiments designed to study the environmental degradation of phenoxyacetic herbicides.

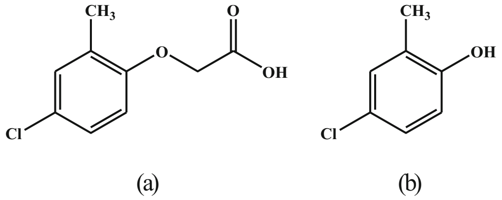
Experimental

Reagents and water samples

Multi-walled carbon nanotubes (MWCNT) were obtained from NanoLab (USA). MCPA, 4-chloro-2-methylphenol, aniline and β-cyclodextrin (β-CD) were supplied by Sigma-Aldrich Química (Sintra, Portugal). All other chemicals and reagents (Sigma-Aldrich Química) employed were of analytical grade and were used as received without any further purification.

All solutions were prepared with deionized water (Milli-Q-50 18 MΩ cm). Buffer solutions employed for voltammetric determinations were 0.1 mol L^{-1} in the pH range 3–9.

HPLC-grade acetonitrile was supplied by Carlo Erba. The solvents were filtered through a 0.45-μm filter before use.



Scheme 1 Molecular structure of **a** MCPA and **b** 4-chloro-2-methylphenol

Environmental water samples were collected from the Leça River Basin located in the north of Portugal. The Leça River is one of the most polluted watercourses in Portugal presenting a high content of organic components. The water samples were obtained from the top metre in 2.5-L brown glass bottles. Once samples arrived at the laboratory, they were filtered through 1-μm glass fibre filters and 0.45-μm cellulose acetate filters, sequentially, to remove suspended particles, and refrigerated at 4 °C prior to use.

Apparatus

Voltammetric experiments were carried out using an Autolab PGSTAT 12 potentiostat/galvanostat (Metrohm Autolab, Netherlands). All measurements were conducted in a one-compartment glass electrochemical cell equipped with a three-electrode system arrangement. The working electrode used was a bare or a modified glassy carbon electrode (GCE, d=2 mm), and the counter electrode was a platinum wire, with a saturated Ag/AgCl reference electrode completing the circuit. All measurements were carried out at room temperature.

The pH measurements were performed using a Crison pH-meter (Crison, Spain) equipped with a glass electrode.

HPLC analysis (Jankowska et al. 2004) was performed using a Shimadzu LC-20 AD Prominence Liquid Chromatograph (Shimadzu, Tokyo, Japan) with a diode array detector (SPD-M20A). Separation was performed on a prepacked Nucleosil 100-5 C18, analytical column (250 mm×4.6 mm, 5 μm, Macherey-Nagel, Duren, Germany), and 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 using the software package LabSolutions (Shimadzu, Japan).

Preparation of MWCNT-modified GCE

The preparation of the PANI-β-CD/functionalised MWCNT (fMWCNT)-modified GCE has been described elsewhere (Rahemi et al. 2012). Two milligrammes of (−COOH) fMWCNT was dispersed by using ultrasonic agitation in 1 mL aqueous β-CD solution (2 %) to give a 2 mg mL^{-1} black suspension. Before surface modification, the 2 mm bare GCE was carefully polished to a mirror with aqueous slurry of alumina powder (BDH Chemicals, VWR, USA) on a microcloth pad and then ultrasonically cleaned in ultra-pure water and ethanol sequentially to remove traces of alumina and possible contaminants. Following this, the cleaned GCE was immersed in a solution containing 0.011 mol L^{-1} aniline and 0.025 mol L^{-1} H_2SO_4 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 deposition of the polyaniline film on the GC electrode surface, an aliquot of 6 μL (2 mg mL^{-1}) of the MWCNT or fMWCNT dispersion was drop cast onto the GCE surface and dried in air at ambient temperature. Finally, the surface of the PANI-β-CD/MWCNT-modified GCE was gently washed with water to remove the loosely attached β-CD/MWCNT.

The PANI-β-CD/fMWCNT film coated GC sensor was activated in phosphate buffer (pH 6) by cyclic voltammetric sweeps between +0.5 and +1.3 V vs. Ag/AgCl until stable cyclic voltammograms were obtained.

For the cleaning of the PANI-β-CD/fMWCNT film coated GC sensor, successive cyclic voltammetric sweeps in 0.1 mol L^{-1} phosphate buffer (pH 6) solution were performed until unchanged cyclic voltammograms were obtained (six cycles).

Photochemical degradation of MCPA

Photodegradation of MCPA in natural water (Leça River) was studied under simulated solar radiation. In order to simulate natural sunlight conditions, a thermostatic chamber equipped with Ultra-Vitalux 300 W (OSRAM) UV–vis lamps (UVA radiated power 315–400 nm 13.6 W and UVB radiated power 280–315 nm 3.0 W) was used. Solutions (100 mL, 0.5 mM) in capped Pyrex flasks were continuously irradiated for 130 h at a fixed distance of 35 cm. Dark controls, consisting of MCPA solutions wrapped in aluminium foil, were also included. Aliquots were collected at specified time intervals and analysed, after proper dilution, using the PANI-β-CD/fMWCNT film coated GC sensor. The amounts of MCPA and 4-chloro-2-methylphenol existing in the solution after irradiation were calculated in both methods based on external calibration. All experiments were carried out in duplicate at 25 ±1 °C.

MCPA and 4-chloro-2-methylphenol assay

For calibration curves, appropriate solutions were prepared by the dilution of aliquots of standard stock solutions of MCPA and 4-chloro-2-methylphenol (10 mM) with the selected pH 6 phosphate buffer supporting electrolyte in order to obtain equimolar concentrations between 10 and 50 μM (10, 20, 30, 40 and 50 μM).

The limit of detection (LOD) was calculated according to IUPAC recommendations (Mocak et al. 1997), using a S/N ratio of three. To verify the accuracy and reproducibility of the method, the results found were compared with those obtained from a previously published HPLC method (Jankowska et al. 2004) and by performing recovery assays. For the latter, known amounts of standard solutions of MCPA and 4-chloro-2-methylphenol were added to the river water samples. The final concentrations of MCPA and 4-chloro-2-methylphenol, after this addition, were 10, 30 and 50 μM.

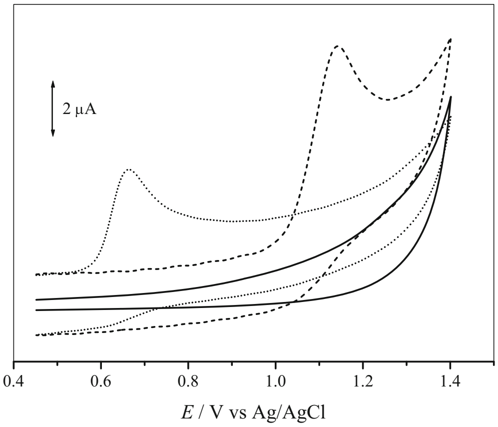


Fig. 1 Cyclic voltammetric responses of PANI-β-CD/fMWCNT/GCE in (*solid line*) pH 6 phosphate buffer electrolyte containing (*dotted line*) 100 μM 4-chloro-2-methylphenol and (*dashed line*) 100 μM MCPA. Scan rate 50 mV s^{-1}

The selectivity of the sensor was investigated by assessing its response to samples of natural river water (Leça River) spiked with increasing amounts of some other herbicides commonly used for the control of broad-leaf weeds. The current responses obtained from the analysis of 4-chloro-2-methylphenol and MCPA without and with the addition of the potentially interfering compounds were compared.

Results and discussion

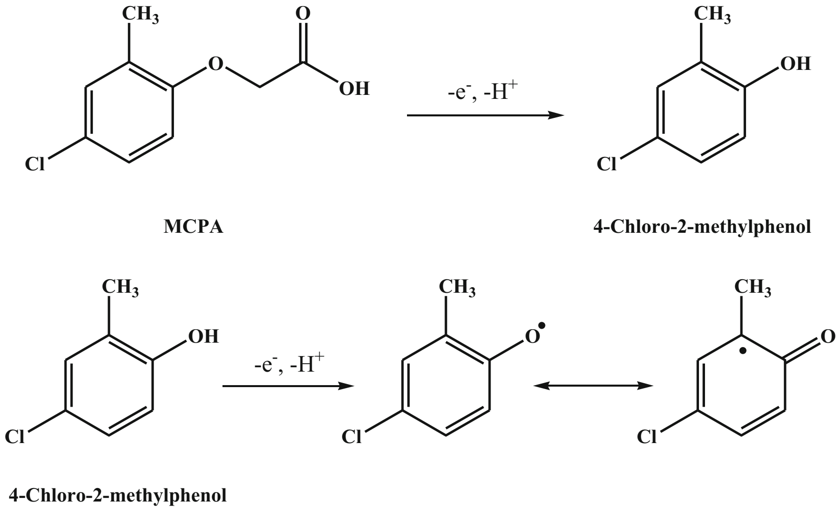
Electrochemical behaviour of MCPA and 4-chloro-2-methylphenol

In our previous study, different GCE surface modifications (PANI/MWCNT, PANI-β-CD/MWCNT and PANI-β-CD/fMWCNT) were investigated in order to assess possible improvements of sensitivity and selectivity of MCPA sensor, using cyclic voltammetry (Rahemi et al. 2012). The results indicated that the PANI-β-CD/fMWCNT-modified glassy carbon electrode exhibits efficient electrocatalytic oxidation of MCPA with high sensitivity, stability and lifetime (Rahemi et al. 2012). Therefore, in this work, the PANI-β-CD/fMWCNT film electrode was selected for the development of a new methodology for the simultaneous determination of MCPA herbicide and its main transformation product 4-chloro-2-methylphenol.

Cyclic voltammograms of MCPA at different pH were obtained at the PANI-β-CD/fMWCNT electrode (Fig. 1). The pH of the supporting electrolyte has a major impact for oxidation of MCPA on modified GCE. From the E_p-pH data obtained, it was concluded that the electrode process is pH-dependent in the interval pH 3 to 9 and that the mechanism of MCPA oxidation in aqueous media proceeds at the aromatic ring, through loss of an electron, forming a cation radical intermediate that undergoes further reaction, namely the cleavage of the ether linkage yielding 4-chloro-2-methylphenol (Scheme 2) (Rahemi et al. 2012). This chlorophenol is also reported in the literature as being the main metabolite of MCPA environmental degradation (Costa et al. 2013; Pozo et al. 2001; Laganà et al. 2002). The effect of pH on the peak current was also investigated, a plot of I_p vs. pH showing that the peak current reaches a maximum around pH 6 (Rahemi et al. 2012).

The voltammetric response of 4-chloro-2-methylphenol was also assessed at the PANI-β-CD/fMWCNT electrode (Fig. 1). Cyclic voltammetry of 4-chloro-2-methylphenol showed an anodic peak at pH 1, at E_p=+0.88 V, corresponding to the oxidation of the phenolic group present in the molecular structure. The E_p-pH plot (Fig. 2) shows that this electrode process is pH-dependent over the whole pH range; E_p decreases linearly with increasing pH. The slope of the dotted line, ca. 60 mV per pH unit, shows that the mechanism of this

Scheme 2 Proposed mechanisms for the electrochemical oxidation of MCPA and 4-chloro-2-methylphenol



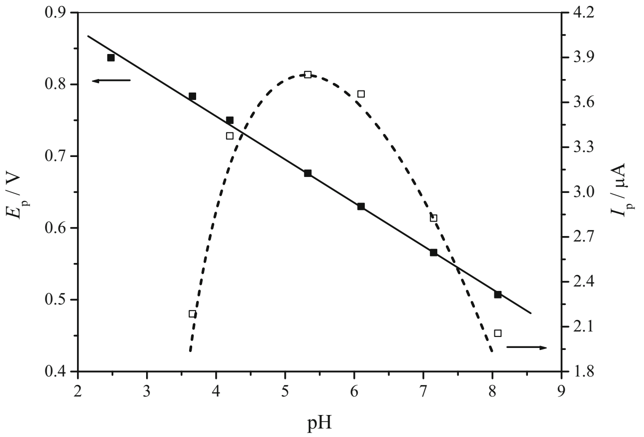


Fig. 2 Plots of E_p (*filled symbols*) and I_p (*open symbols*) vs. pH from cyclic voltammograms of 0.1 mM solutions of 4-chloro-2-methylphenol at PANI-β-CD/fMWCNT film electrode in different buffer electrolytes as a function of pH. Scan rate 50 mV s^{-1}

oxidation process in aqueous media involves the same number of electrons and protons. At pH values higher than 9, a significant decrease in the oxidation current was observed. This seems to be directly related with the ionization constant of 4-chloro-2-methylphenol (pK_a=9.71) (United Nations 1998). The voltammetric behaviour observed is consistent with the oxidation mechanism suggested in the literature for phenols. The first step in the electrooxidation of 4-chloro-2-methylphenol should involve a one-electron transfer with formation of a phenoxy radical (Scheme 2). The phenoxy radical can subsequently react in at least two ways: in one pathway, the radical initiates an irreversible dimerization process due to a radical-radical coupling reaction between two phenoxy radicals; and in the other, the radical can be further oxidized to a quinone-like structure (Lund and Baizer 1991; Ureta-Zanãrtu et al. 2002).

The effect of electrolyte pH on the 4-chloro-2-methylphenol oxidation peak current was also investigated. A plot of I_p vs. pH indicates that the peak current reaches a maximum around pH 5 (Fig. 2). Although the highest peak current is observed at pH 5, it was decided to perform all subsequent analytical experiments using pH 6 phosphate buffer supporting electrolyte. This choice is the most favourable for MCPA determination (Rahemi et al. 2012), there is only a slight decrease (ca. 3 %) in the peak current of 4-chloro-2-methylphenol compared with pH 5, and pH 6 buffer leads to the longest operational lifetime of the PANI-β-CD/fMWCNT/GC-modified electrode (Rahemi et al. 2012).

The influence of scan rate on the peak current of MCPA and 4-chloro-2-methylphenol was investigated in pH 6 phosphate buffer solution. In both cases, the peak current increases linearly with square root of scan rate, in the range of 10–150 mV s^{-1}. The results found confirm the electrode reaction mechanisms for MCPA and 4-chloro-2-methylphenol oxidation at the PANI-β-CD/fMWCNT film-modified electrode and that both exhibit the influence of diffusion of the electroactive species in solution to the modified electrode surface.

The simultaneous CV determination of MCPA and 4-chloro-2-methylphenol was therefore carried out scanning the potential from +0.5 to +1.4 V in 0.1 mol L^{-1} phosphate buffer solution (pH 6.0), containing 100 μM of MCPA, 100 μM of 4-chloro-2-methylphenol or an equimolar mixture of both compounds. Figure 3 depicts the CV response for an MCPA and 4-chloro-2-methylphenol equimolar mixture, obtained using a scan rate of 50 mV s^{-1} at the bare GC electrode (curve A) and at PANI-β-CD/fMWCNT (curve B). The results obtained show that, over the potential range studied, there is only one oxidation wave for each of the compounds with no corresponding reduction wave on scan reversal, suggesting that the electrochemical reactions are both totally irreversible processes. The electrochemical responses of 4-chloro-2-methylphenol and MCPA at the bare GC electrode are rather small (curve A), presenting broad and small anodic waves at 0.661 and 1.181 V, respectively.

Compared to the bare GC electrode, at the PANI-β-CD/fMWCNT-modified electrode, the peak potentials of 4-chloro-2-methylphenol and MCPA are shifted to less positive potentials (by about 40 mV) which suggests that the film promotes the electrochemical reaction of both compounds more efficiently. The greatly enhanced peak currents can be attributed to the use of functionalised MWCNT, related to the increase of the electroactive area of the carbon nanotubes, and also to an increase of the local concentration of 4-chloro-2-methylphenol-β-CD and MCPA-β-CD in the PANI-β-CD/MWCNT film due to the ability of β-cyclodextrin to form inclusion complexes with these organic molecules.

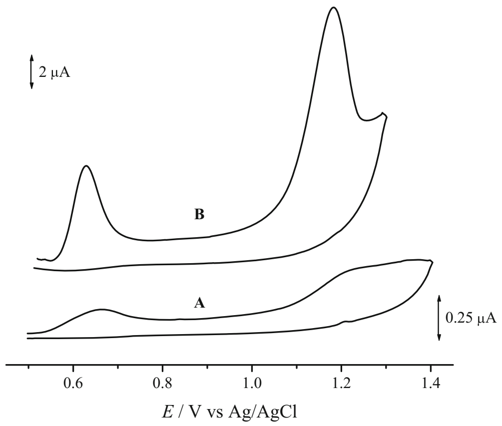


Fig. 3 Cyclic voltammograms of an equimolar (100 μM) mixture solution of MCPA and 4-chloro-2-methylphenol at (*a*) GCE and (*b*) PANI-β-CD/fMWCNT/GCE in pH 6 phosphate buffer electrolyte. Scan rate 50 mV s^{-1}

Simultaneous determination of MCPA and 4-chloro-2-methylphenol

CV experiments were performed in triplicate using the optimized experimental parameters to construct an analytical curve for the determination of MCPA and 4-chloro-2-methylphenol at the PANI-β-CD/fMWCNT film electrode.

Cyclic voltammograms recorded with increasing amounts of 4-chloro-2-methylphenol and MCPA (10 to 50 μM) showed that the peak currents increase linearly with increasing concentration (Fig. 4). Analytical data for the calibration plots are summarized in Table 1. The limit of detection (LOD) obtained from five runs for 4-chloro-2-methylphenol and MCPA was 1.9 and 1.1 μM, respectively. The precision of the method was evaluated by repeatedly (n=5) measuring 4-chloro-2-methylphenol and MCPA, at three levels of concentration (10, 30 and 50 μM) on the same day and over five consecutive days (Table 1). The maximum value of the inter-day precision obtained, expressed as coefficient of variation, was approximately 3 %.

The proposed method was applied to the analysis of both compounds in river water spiked with 4-chloro-2-methylphenol and MCPA, using the standard addition method, in order to eliminate any matrix effects. Cyclic voltammograms obtained from the determination of 4-chloro-2-methylphenol and MCPA in river water samples are presented in Fig. 4 (inset). The recoveries obtained were satisfactory, as shown in Table 2.

Table 1 Linearity range, detection limits and inter-day repeatability for determination of 4-chloro-2-methylphenol and MCPA, using the cyclic voltammetric method (CV), in pH 6 phosphate buffer electrolyte

	CV	
	4-Chloro-2-methylphenol	MCPA
Linearity range (μM)	10–50	10–50
Calibration plot (n=5)		
Intercept (μA)	0.204	0.273
Slope (A M^{-1})	0.103	0.182
Correlation coefficient	0.992	0.996
Standard error of intercept	0.158	0.277
Standard error of slope	0.005	0.009
Inter-day precision (n=5)[a]		
10 μM	2.65	2.62
30 μM	2.12	2.93
50 μM	2.44	2.05
LOD (μM)	1.92	1.06

[a] Precision as coefficient of variation (CV, %)=standard deviation divided by mean measured concentration × 100

The accuracy of the voltammetric method was assessed by comparing the results found with those obtained using a previously published chromatographic procedure (Jankowska et al. 2004). Five independent measurements were carried out, for both the CV and HPLC methods. These results, summarized in Table 2, show that the data from the CV method agree well with those from chromatography. The F- and t tests were carried out on the data, and the validity of the results obtained was statistically examined. At a confidence level of 95 %, the values from the t and F-tests were less

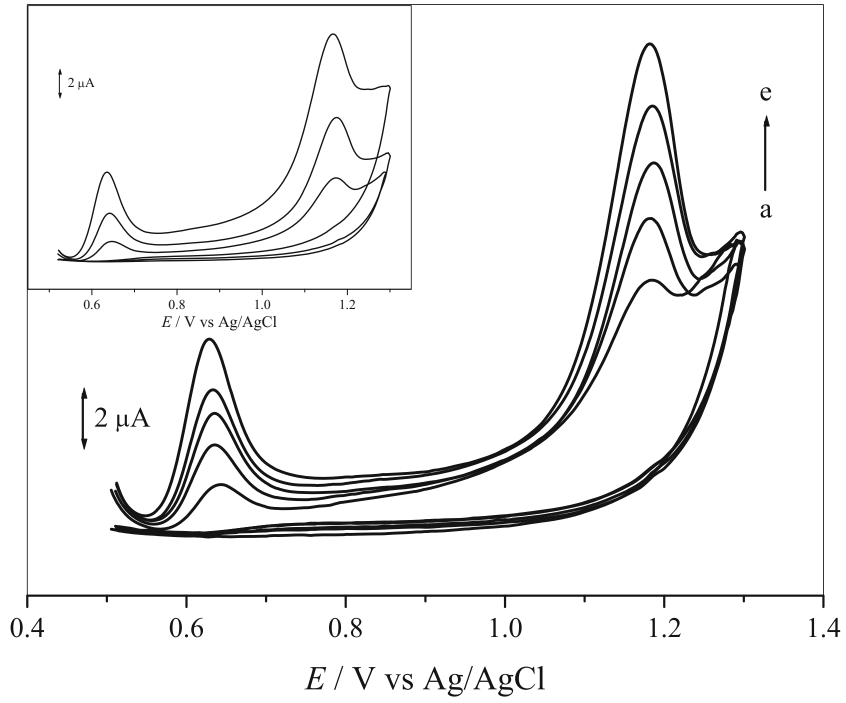


Fig. 4 Cyclic voltammograms of MCPA and 4-chloro-2-methylphenol equimolar standard solutions with concentrations of (*a*) 10, (*b*) 20, (*c*) 30, (*d*) 40 and (*e*) 50 μM at PANI-β-CD/fMWCNT film electrode in pH 6 phosphate buffer electrolyte. Scan rate 50 mV s^{-1}. *Inset*: cyclic voltammograms obtained for the determination of MCPA and 4-chloro-2-methylphenol at equimolar concentrations of 10, 30 and 50 μM in spiked river water samples. Scan rate 50 mV s^{-1}

Table 2 Results obtained for the analysis of 4-chloro-2-methylphenol and MCPA in river water samples using the proposed cyclic voltammetric (CV) method and HPLC

Method	4-Chloro-2-methylphenol		MCPA	
	CV	HPLC	CV	HPLC
Added (μM)	10	10	10	10
	30	30	30	30
	50	50	50	50
Found (μM)	10.2	9.9	10.5	10.7
	29.3	30.4	28.2	28.9
	52.1	51.4	49.9	51.4
Recovery (%)[a]	102.0	99.0	105.0	107.0
	97.7	101.3	94.0	96.3
	104.2	102.8	99.8	102.8
RSD (%)	1.89	2.55	4.01	4.74
	2.07	2.56	4.80	4.16
	2.72	2.96	1.72	2.07
t test[b]	1.90		0.60	
	2.23		0.80	
	0.67		2.19	
F-test[b]	1.70		1.44	
	1.65		1.26	
	1.15		1.53	

[a] Average of five replicate measurements

[b] Tabulated *t* and *F* values, at P=0.05, are 2.31 and 6.39, respectively

than the theoretical values, showing that there is no significant difference between the proposed CV technique and the HPLC method.

The results reveal that both methodologies have comparable precision and accuracy. However, the PANI-β-CD/fMWCNT film electrode proposed in the present paper shows a significant improvement in terms of simple preparation and low cost.

Monitoring of photodegradation of MCPA in natural water

The new voltammetric methodology based on PANI-β-CD/fMWCNT film electrode was applied to the monitoring of the photodegradation process of MCPA in natural water.

The photodegradation of MCPA in aqueous solution is shown in Fig. 5, plotting the concentration of remaining herbicide vs. irradiation time. The MCPA photodegradation profile followed an exponential decay, corresponding to simple first-order kinetics. No disappearance of MCPA was detected in the dark experiments, demonstrating that the disappearance of the herbicide was due only to photodegradation, permitting exclusion of other phenomena such as volatilization or thermal degradation.

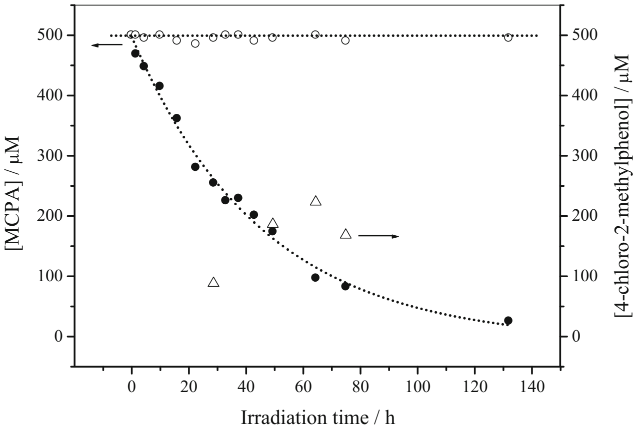


Fig. 5 Photodegradation of MCPA in river water under (*filled circle*) simulated solar irradiation and (*open circle*) dark conditions. Time evolution (*open triangle*) of 4-chloro-2-methylphenol concentration upon simulated solar irradiation

The presence of 4-chloro-2-methylphenol, produced during irradiation, was also monitored (Fig. 5). The results showed that the amount of 4-chloro-2-methylphenol formed increased until 65 h of irradiation and then started to decrease, probably due to its own degradation (Bojanowska-Czajka et al. 2006).

Selectivity and stability of PANI-β-CD/fMWCNT/GC

The selectivity and stability play an important role in continuous environmental monitoring. The stability of the PANI-β-CD/fMWCNT/GC-modified electrode was tested over a 5-day period. Cyclic voltammetry of 4-chloro-2-methylphenol and MCPA at the modified electrode showed that the oxidation peak potentials remained unchanged, and the initial anodic peak currents were maintained during this period, with relative standard deviations lower than 6 %.

To investigate the effects of common interfering substances on the determination of MCPA and 4-chloro-2-methylphenol in natural waters with the use of the novel sensor, controlled amounts of the interfering substances were added individually to a river water sample containing an equimolar mixture (30 μM) of MCPA and 4-chloro-2-methylphenol. Thus, different amounts of Ca^{2+}, Mg^{2+}, NO_3^-, PO_4^{3-} and some other herbicides commonly used for the control of broad-leaf weeds, i.e. 2,4-D, dicamba, atrazine and glyphosate, were investigated for possible interferences. At mass ratios of 1:1, no significant interference was observed (signal change less than 5 %) (Fig. 6). The interference of 4-chloro-2-methyl-6-nitrophenol, often referred to in the literature as an important environmental transformation intermediate of 4-chloro-2-methylphenol (Chiron et al. 2009), was not tested owing to the difficulty of obtaining this compound commercially. The synthesis of 4-chloro-2-methyl-6-nitrophenol is currently in progress in order to investigate the electrochemical properties

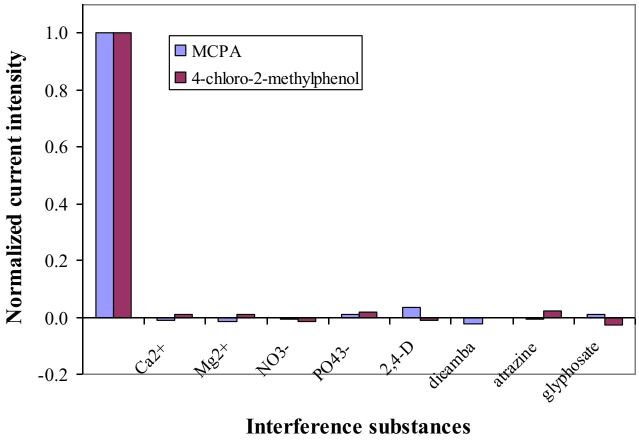


Fig. 6 Normalized current ratios representing the effect of various interfering substances on the oxidation peak currents corresponding to 4-chloro-2-methylphenol and MCPA (all at a concentration of 30 μM) at PANI-β-CD/fMWCNT film electrode in pH 6 phosphate buffer electrolyte. Normalized current=$(I-I_0)/I_0$, where I and I_0 represent the measured and the original current, respectively

of this compound using the PANI-β-CD/fMWCNT/GC-modified electrode and to assess its possible interference in the simultaneous determination of 4-chloro-2-methylphenol and MCPA.

Conclusions

A new electroanalytical procedure is proposed for the simultaneous monitoring of the herbicide MCPA and its main degradation product 4-chloro-2-methylphenol in natural waters, based on the use of a PANI-β-CD/fMWCNT/GC-modified electrode. The electrochemical sensor developed showed good electrochemical characteristics and analytical performance. The results show that the new methodology is a good alternative to the chromatographic method (HPLC), frequently used for determining pesticides and their transformation products.

The PANI-β-CD/fMWCNT/GC film showed electrocatalytic behaviour towards the herbicide MCPA and its main degradation product 4-chloro-2-methylphenol and enabled its determination in real environmental samples with good sensitivity, not requiring separations or derivatization steps, which are indispensable in many other analytical methodologies. The method is selective: interferences from ionic species and from other herbicides used for broad-leaf weed control were shown to be small.

In addition to the demonstrated suitability of the PANI-β-CD/fMWCNT/GC electrode as a sensor for rapid and sensitive screening of herbicide residues, these new findings suggest that the combination of host–guest electrostatic interactions with the catalytic and electronic properties of MWCNT represents an interesting and useful method for simultaneous screening of herbicides and some of their transformation products.

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