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Direct electrochemical determination of carbaryl using a multi-walled carbon nanotube/cobalt phthalocyanine modified electrode

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ABSTRACT

The electrochemical detection of carbaryl at low potentials, in order to avoid matrix interferences, is an important challenge. This study describes the development, electrochemical characterization and utilization of a glassy carbon (GC) electrode modified with multi-wall carbon nanotubes (MWCNT) plus cobalt phthalocyanine (CoPc) for the quantitative determination of carbaryl in natural waters. The surface morphology was examined by scanning electron microscopy, enhanced sensitivity was observed with respect to bare glassy carbon and electrocatalytic effects reduced the oxidation potential to +0.80 V vs. SCE in acetate buffer solution at pH 4.0. Electrochemical impedance spectroscopy was used to estimate the rate constant of the oxidation process and square-wave voltammetry to investigate the effect of electrolyte pH. Square-wave voltammetry in acetate buffer solution at pH 4.0, allowed the development of a method to determine carbaryl, without any previous step of extraction, clean-up, or derivatization, in the range of 0.33–6.61 μmol L^{-1}, with a detection limit of 5.46 ± 0.02 nmol L^{-1} (1.09 ± 0.02 μg L^{-1}) in water. Natural water samples spiked with carbaryl and without any purification step were successfully analyzed by the standard addition method using the GC/MWCNT/CoPc film electrode.

1. Introduction

Carbamate compounds are the most widely used pesticides due to their high insecticidal activity and relatively low persistence [1]. Carbaryl (1-naphthyl methylcarbamate) was the first successful carbamate insecticide; it is broad-spectrum and used to control over 100 species of insect on crops, on lawns, ornamental plants, trees, in forestry and even on animals. It is also used as a molluscicide and acaricide [2]. Considered a short-lived pesticide, the mode of action of carbaryl in vertebrates and insects is based on inhibition of the activity of acetylcholinesterase (AChE) enzyme in the hydrolysis of the neurotransmitter acetylcholine, which is responsible for the transmission of nervous impulses [3].

The indiscriminate use of carbaryl can cause its bioaccumulation in food and water sources with subsequent bio-concentration through the food chain. In humans, acute and chronic occupational exposure has been observed to cause inhibition of cholinesterase and reduced enzyme activity in the blood, leading to neurological effects, nausea, vomiting, coma, respiratory failure and death [4]. The maximum residue levels of pesticides in food, water and vegetable samples are regulated by government agencies of most countries. Thus, sensitive and rapid determination of these compounds is important for the protection of the environment and of human health.

Most of the analytical methods employed for the determination of carbaryl have been based on chromatographic techniques using different detection systems [5,6]. These methods do not easily allow continuous in situ analysis and often require several previous steps in sample preparation, which include an extraction and clean-up procedure in order to obtain a final extract fully compatible with chromatographic determination. These techniques usually generate waste-containing organic solvents, which makes the procedure more complicated and more expensive.

Electrochemical methods have the advantage of low cost, high sensitivity, easy operation, potentiality for miniaturization and automation, construction of simple portable devices for fast screening purposes and in-field/on-site monitoring. Several electrochemical methods to quantify carbaryl have been reported. These indirect methods are based on amperometric or voltammetric detection using the inhibition of acetylcholinesterase enzyme [7,8]. However, the use of enzymes as modifiers of electrodes needs special care with respect to pH, temperature, applied potential, storage, and enzyme activity, which makes these systems more difficult to work with and less robust.

The direct electrochemical detection of carbaryl without derivatization was first reported by Rao et al. [9]. In 2006, Codognoto et

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al. [10] developed a methodology to quantify carbaryl in natural waters. In both cases, a boron doped diamond (BDD) electrode was used to oxidize carbaryl at the amide nitrogen in the carbamate molecule, that usually occurs at high potentials [11]. The carbaryl oxidation potential of 1.4 V at BDD is thus subject to the interference of many substances, especially in environmental matrices. In this sense, exploring the use of carbon nanotubes becomes an interesting alternative, as an electrocatalytic material to reduce the oxidation potential, for the direct electrochemical determination of carbaryl.

Since their discovery in 1991 [12], carbon nanotubes (CNTs) have been the target of numerous investigations, owing to their extraordinary mechanical, chemical and electronic properties [13]. The CNT mechanism of charge transport can vary from semiconducting-type to metallic-type depending on their radius and helical structure and ability to mediate electron transfer reactions with electroactive species in solution [14]. They have been studied extensively for a large variety of applications, particularly for solid-state chemical and biological sensors [15]. The development of new materials for electrochemical sensors with improved reproducibility, sensitivity and stability is one of the areas of greater and faster growth in materials science [16].

Metallophthalocyanine complexes (MPc) are well recognized for their excellent electrocatalytic activity in many reactions, which is highly dependent on the central metal atom (as well as on substituents in the case of aza-macrocyclic compounds). The change in the geometry of the complex during the redox process is one of the most important factors to be considered [17]. It is possible for phthalocyanines to be a convenient substitute for natural proteins, since they can act as the active centre of an enzyme molecule with the same efficiency and selectivity [18].

It is known that amino-substituted metallophthalocyanine complexes can be covalently linked to CNTs via amide bond formation [19] while non-substituted MPc complexes are non-covalently adsorbed onto CNTs via π–π interactions. It has been observed that phthalocyanine–CNT complexes have the excellent catalytic properties of phthalocyanines without losing any of the electronic properties of carbon nanotubes [20,21]. In recent work, Moraes et al. development an electrochemical device using phthalocyanine-functionalized carbon nanotubes as a sensor for dopamine contaminated with a high concentration of ascorbic acid, reaching a detection limit of 2.6×10^{-7} mol L^{-1} [22].

In the study reported here, a glassy carbon (GC) electrode surface-modified with multi-walled carbon nanotubes plus cobalt phthalocyanine (MWCNT/CoPc) was employed for the direct oxidative determination of carbaryl in pure and natural water samples using square-wave voltammetry (SWV).

2. Experimental

2.1. Apparatus and procedures

Square-wave voltammetry (SWV) experiments were performed using a μAutolab Type III PGSTAT (Eco Chemie, Utrecht, Netherlands) potentiostat/galvanostat coupled to a personal computer and controlled with GPES 4.9 software. The electrochemical cell was assembled with a conventional three-electrode system: bare glassy carbon (GC) (3.0 mm diameter), glassy carbon modified with multi-walled carbon nanotubes (GC/MWCNT), or a glassy carbon modified with multi-walled carbon nanotubes plus cobalt phthalocyanine (GC/MWCNT/CoPc), saturated calomel (SCE) as reference and a Pt wire as auxiliary electrode. All experiments were carried out at room temperature (25 ± 1 °C).

A 1.0×10^{-2} mol L^{-1} stock solution of carbaryl (99.8% purity, Sigma–Aldrich, Germany), was prepared daily in acetonitrile (J.T. Baker, chromatographic grade, Netherlands). Aliquots of this stock solution were diluted in aqueous electrolyte solution for the voltammetric experiments up to a maximum final concentration of 0.20 mmol L^{-1} (500 μL of acetonitrile solution in 25 mL of electrolyte). Solutions of buffer supporting electrolyte (acetic acid/acetate buffer pH 3.1, 4.0 and 5.0; sodium phosphate buffer pH 6.2 and 7.0; borate buffer pH 9.0) of ionic strength 0.1 mol L^{-1} were used in all experiments, and were prepared using analytical grade reagents and purified water from a Millipore Milli-Q system (conductivity <0.1 μS cm^{-1}).

The SWV measurements were performed using a frequency of 20 Hz, amplitude of 100 mV and step potential of 2 mV in 0.1 mol L^{-1} of acetate buffer solution (pH 4.0) for carbaryl calibration curves.

Electrochemical impedance spectroscopy (EIS) data were obtained using a PC-controlled Solartron 1250 Frequency Response Analyzer coupled to a Solartron 1286 Electrochemical Interface using ZPlot 2.4 software (Solartron Analytical, UK), scanning from 65 kHz to 100 mHz frequency range and 10 mV amplitude, with 10 data points per frequency decade. The impedance spectra were recorded within the potential range for the carbaryl oxidation process, in 0.1 mol L^{-1} acetate buffer solution (pH 4.0) containing 5.0×10^{-3} mol L^{-1} of carbaryl stock solution.

2.2. Preparation of the electrodes

MWCNT (90% purity, Sigma–Aldrich) synthesized by thermal chemical vapor deposition were mixed with 1.0 g of MWCNT per 500 mL of a 1:3 mixture of HNO_3/H_2SO_4 for 12 h, in order to promote functionalisation. They were then filtered through a 0.45 μm Millipore nylon filter membrane. The resulting MWCNT were continuously washed using distilled water until the pH of the filtrate was neutral and then dried overnight in a vacuum oven at 120 °C.

Prior to modification, the glassy carbon electrode surface was polished with 0.5 μm alumina slurry, rinsed thoroughly with ultra-pure water, sonicated 3 min in acetone and 3 min in water, and dried in air. For MWCNT, a mass of 2.0 mg of MWCNT was dispersed in 1.0 mL dimethylformamide (DMF) using ultrasonic stirring for 20 min. For MWCNT/CoPc, 2.0 mg of treated MWCNT plus 1.0 mg of CoPc (Sigma–Aldrich) was dispersed by ultrasonic stirring for 20 min in 1.0 mL of DMF. A 10 μL aliquot of one or the other dispersion was placed as a droplet on the GC electrode surface and the solvent was then left to evaporate at room temperature. DMF was used because it was found to be more compatible than other solvents (ethanol, acetone, etc.) with the hydrophobic nature of the GC surface and led to a more homogeneous film.

The GC, and the MWCNT and MWCNT/CoPc modified electrodes, were characterized using a Field Emission Gun with Scanning Electron Microscopy (FEG-SEM) using a FEG-Zeiss model Supra 35VP (Zeiss, Germany), by SWV and by EIS.

2.3. Recovery experiments

The standard addition method was used to test the developed methodology in spiked river water. For this purpose, river water samples were spiked with 1.66 μmol L^{-1} of carbaryl and the square-wave voltammetry signal recorded. After that, three additions of equal amounts of carbaryl were performed up to a final carbaryl concentration of 3.32 μmol L^{-1}. Extrapolation of the resulting linear regression plot gave the recovery amount of carbaryl in the spiked river water samples.

3. Results and discussion

3.1. Surface morphology of the modified electrodes

The morphology of the modified electrodes was examined by FEG-SEM. Fig. 1 displays typical images of MWCNT

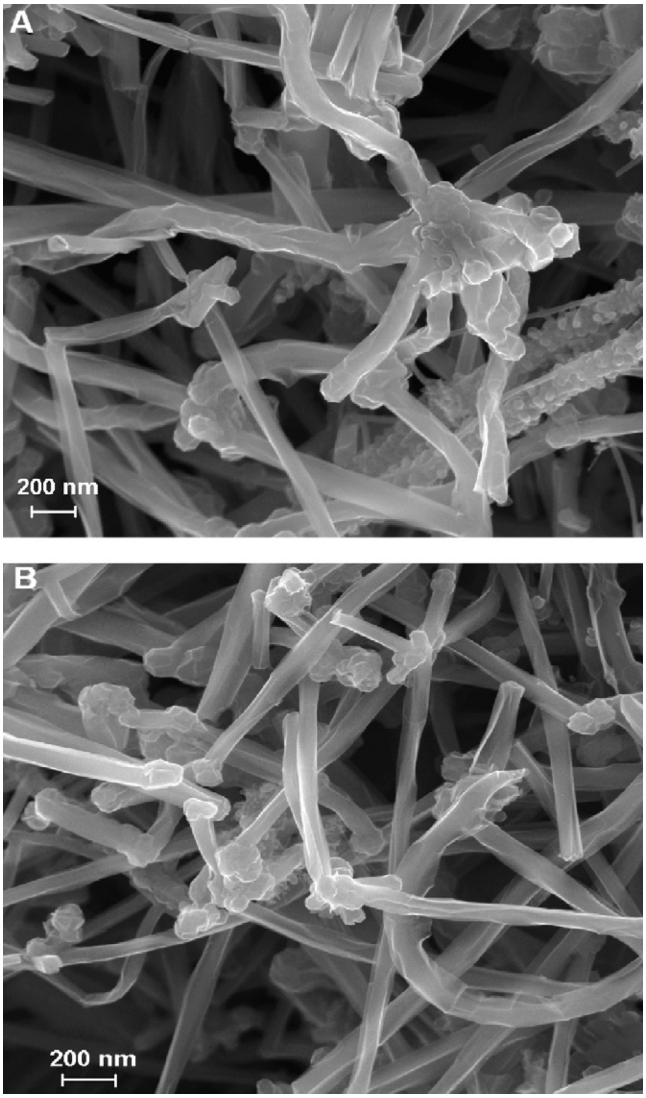


Fig. 1. FEG-SEM micrographs for (A) MWCNT and (B) MWCNT/CoPc films.

and MWCNT/CoPc films assembled onto GC electrodes. The functionalized MWCNT and MWCNT/CoPc films are uniformly distributed. Fig. 1A shows that the MWCNT have average length and radius of 0.5 μm and 80 nm, respectively, and completely cover the GC surface. In Fig. 1B it can be seen that for MWCNT/CoPc, the cobalt phthalocyanine is preferentially adsorbed onto the ends of the MWCNT cylinders. This process of adsorption is in agreement with the fact that phthalocyanines can be covalently linked to CNTs via amide bond formation [19].

3.2. Electro-oxidation of carbaryl

The study of carbaryl electro-oxidation was carried out by SWV, scanning the potential from +0.5 to +1.45 V in 0.1 mol L^{-1} acetate buffer solution (pH 4.0), containing 1.0×10^{-4} mol L^{-1} of carbaryl.

Fig. 2 shows SW voltammograms at all three types of electrode and demonstrates that, in the potential range studied, there is only one oxidation process. On the GC/MWCNT film electrode, carbaryl oxidation occurred at +0.98 V, which is 0.28 V less positive than on a bare GC electrode, showing the electrocatalytic effect of the CNTs. Moreover, the oxidation on such a catalytic surface showed a factor of 3.3 increase in the peak current compared with the bare GC electrode, which can be related to the high surface area of the carbon nanotubes.

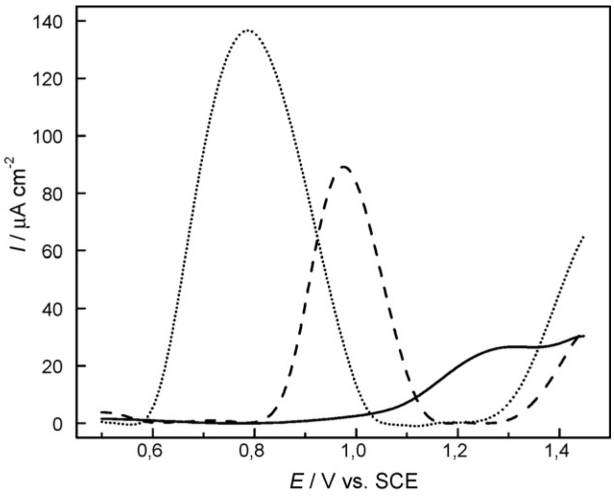


Fig. 2. Square-wave voltammograms in 0.1 mol L^{-1} acetate buffer solution (pH 4.0), containing 1.0×10^{-4} mol L^{-1} of carbaryl for bare GC (solid line), GC/MWCNT film (dashed line) and GC/MWCNT/CoPc film (dotted line) electrodes.

On the GC/MWCNT/CoPc film electrode, the carbaryl oxidation potential decreases to +0.80 V, i.e. by a further 0.18 V with respect to the GC/MWCNT film electrode. The extra factor of 1.5 increase in peak current can be associated with more efficient adsorption due to the phthalocyanine. Using this electrode, any interferents oxidising above 1.0 V will be effectively excluded from the carbaryl measurement. Thus, the electrocatalytic properties of carbon nanotubes are added to the excellent electron mediator power of cobalt phthalocyanines to make the synergistic system GC/MWCNT/CoPc a promising setup for direct carbaryl electrochemical detection.

3.3. Electrochemical impedance spectroscopy

The EIS experiments allow obtaining the charge-transfer resistance values for the electrode process. Spectra recorded at potentials where carbaryl oxidation occurs: bare GC electrode +1.25 V, GC/MWCNT film electrode +0.92 V and GC/MWCNT/CoPc film electrode +0.75 V, are shown in the complex plane format in Fig. 3. They consist of semicircles at high to medium frequencies and a straight line at low frequencies, corresponding to kinetic and diffusion control, respectively.

The spectra in Fig. 3 were modelled using the modified Randles equivalent circuit consisting of the cell resistance R_Ω, in series with a parallel combination of a constant phase element CPE considered as a non-ideal capacitance of capacity C with CPE exponent α, where $\alpha = 1$ represents a perfectly smooth and homogeneous surface and a charge-transfer resistance R_{ct}, with a Warburg impedance Z_W (domain of mass transport control), resulting from the diffusion of carbaryl towards the electrode surface from the bulk of the electrolyte. The fitting parameters obtained are listed in Table 1. As expected [23], the R_Ω values are very similar for the three different types of electrode. The capacitance values increase at the GC/MWCNT/CoPc and GC/MWCNT film electrodes compared with bare GC, probably related to the increase in surface area of the elec-

Table 1
Summary of calculated EIS parameters obtained for the electrodes.

Electrodes	R_Ω/kΩ cm^2	C/μF cm^{-2} s$^{\alpha-1}$	α	R_{ct}/kΩ cm^2	k_{app}/cm s^{-1}
Bare GC	0.097	7.80	0.81	2.72	1.95×10^{-5}
GC/MWCNT	0.103	35.4	0.75	1.05	5.04×10^{-5}
GC/MWCNT/CoPc	0.094	65.2	0.74	0.42	1.26×10^{-4}

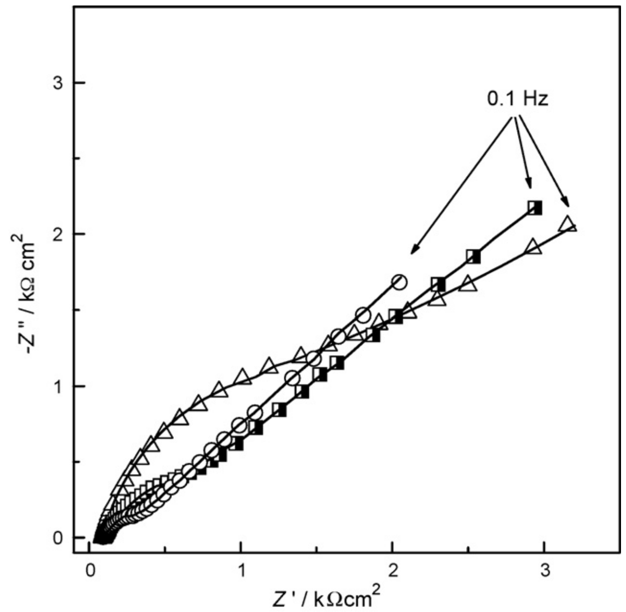


Fig. 3. Complex plane impedance spectra at bare GC (△), GC/MWCNT (■), and GC/MWCNT/CoPc (○), in 0.1 mol L^{-1} acetate buffer solution (pH 4.0), containing 1.0×10^{-4} mol L^{-1} of carbaryl. The solid lines show fitting to the equivalent circuit described in the text.

trode. Apparent standard rate constants, k_{app}, were calculated from the equation [24]:

$$k_{app} = \frac{RT}{F^2 R_{ct} c} \quad (1)$$

where c is the carbaryl concentration (in mol cm^{-3}) and R, T and F have their usual meanings. As indicated by the large decrease in the R_{ct} values (Table 1), the GC/MWCNT/CoPc electrode exhibited a faster charge-transfer process towards carbaryl oxidation than the other electrodes investigated. Apparent standard rate constants, k_{app}, for oxidation at the GC/MWCNT/CoPc, GC/MWCNT and for the bare GC, determined from the impedance spectra, were 1.26×10^{-4}, 5.04×10^{-5} and 1.95×10^{-5} cm s^{-1}, respectively.

3.4. *Optimization studies of carbaryl on the GC/MWCNT/CoPc film electrode*

To maximize the SWV analytical signal, the effects of the experimental parameters (pre-treatment cleaning potential and time, pH, pulse amplitude, frequency and potential step height) were studied at the GC/MWCNT/CoPc film electrode, using 0.1 mol L^{-1} acetate buffer, at pH 4.0 unless otherwise stated, containing 1.0×10^{-4} mol L^{-1} of carbaryl.

3.4.1. *Study of pre-treatment potential and time for cleaning the electrode surface*

In general, the electrochemical detection of pesticides is accompanied by adsorption of the pesticide or its oxidation products [25]. Thus, there is a poisoning of the electrode surface and consequent decrease of the analytical signal. The influence of applied potential pre-treatment after each scan was investigated, in order to clean the surface of the electrode. The following pre-treatment potential values: −1.0, −0.75, −0.50, −0.25, 0.0 and 0.25 V were investigated, and the results are shown in Fig. 4.

Complete recovery of the original response was obtained between −1.0 and −0.5 V. At more positive cleaning potentials the peak current, I_{pa}, obtained during the following experiment begins to decrease, reaching only 30% at +0.25 V pre-treatment cleaning potential. Thus, −0.50 V was chosen as the pre-treatment cleaning potential in further studies.

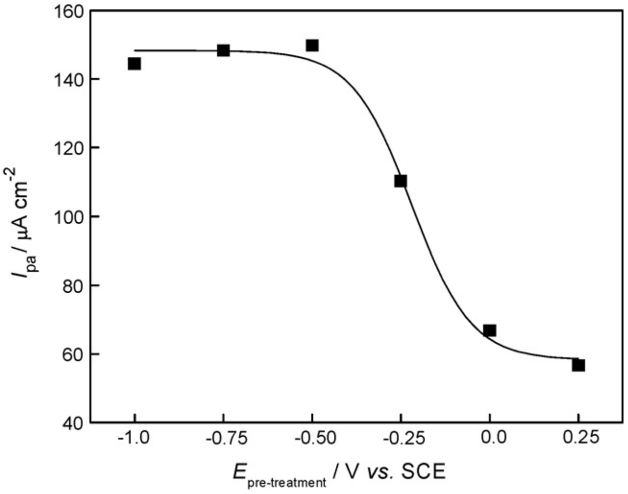


Fig. 4. Effect of pre-treatment potential on the carbaryl oxidation peak current in 0.1 mol L^{-1} acetate buffer solution (pH 4.0), containing 5.0×10^{-3} mol L^{-1} of carbaryl, with the optimized SWV parameters.

The influence of the pre-treatment time was also evaluated, varying it from 10 to 60 s, and in this interval no difference was seen. Hence 10 s was chosen as time of pre-treatment for cleaning the electrode surface.

3.4.2. *Effect of electrolyte pH*

The dependence of the electrochemical oxidation of carbaryl on the pH was studied by square-wave voltammetry in the pH range from 3.0 up to 9.0 plus 1.0×10^{-4} mol L^{-1} of carbaryl. The results obtained are shown in Fig. 5, which is a plot of the SWV peak current (I_{pa}) and peak potential (E_{pa}) as a function of pH.

The variation of E_{pa} with pH can provide valuable information on the carbaryl oxidation process. The increase in pH causes a shift in the peak potential towards less positive values, the slope of the E_{pa} vs. pH plot being 53 mV per pH unit, so that it can be concluded that the same number of protons and electrons is involved in the carbaryl oxidation process. Additionally, the SWV carbaryl oxidation peak half-width, $W_{1/2}$, is greater than 90 mV, which would suggest a one-electron oxidation and thence one proton. Further, in [26] it is stated that the nitrogen atom is protonated up to approximately pH 6, from which one proton can be released on oxidation and so

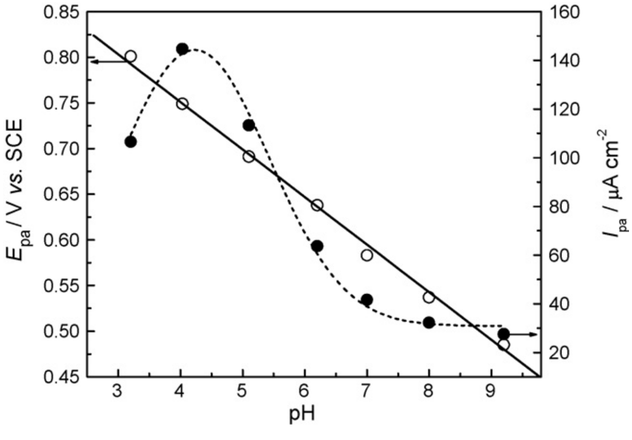
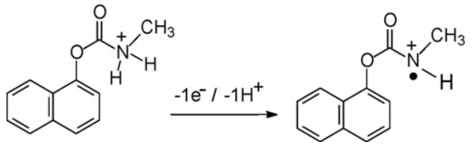


Fig. 5. Effect of pH on the peak potential (○) and peak current (●) for carbaryl oxidation on the GC/MWCNT/CoPc film electrode using buffer supporting electrolyte of ionic strength 0.1 mol L^{-1}, containing 1.0×10^{-4} mol L^{-1} of carbaryl.



Scheme 1. Electrochemical reaction mechanism of carbaryl oxidation.

the loss of one electron is inferred also by this reasoning. Based on the above considerations, the electrochemical oxidation of carbaryl could proceed as illustrated in Scheme 1; the product is a cation radical which, after losing a further proton, can adsorb on the phthalocyanine or undergo dimerisation or polymerisation.

The plot of I_{pa} vs. pH shows that the peak current has a maximum value at pH 4.0 decreasing for both higher and lower pH values. At low pH values the nitrogen of the carbaryl molecules is protonated, and above pH 9.0 it is hydrolysed to naphthol [26]. The peak current behaviour observed in this work is unexpected due to the maximum at pH 4. However, it must be remembered that, the carbaryl molecule should interact with the phthalocyanine active site on the electrode surface. As this modifier molecule also protonates itself at low pH values, the overall effect can result in that observed here, i.e., diminishing of peak current. This behaviour has already been seen for the dopamine/phthalocyanine system [22]. Thus, pH values around 4 should provide the highest oxidation currents justifying the selection of pH 4.0 for the subsequent experiments using the GC/MWCNT/CoPc film electrode.

3.4.3. Optimization of SWV conditions

The influence of square-wave voltammetry parameters was investigated. First, the amplitude was varied in the range of 10–100 mV, fixing the frequency at 50 Hz and I_{pa} increased with increasing amplitude in this range. No deformation of the peak was observed nor any significant increase in peak width, even for amplitudes greater than 50 mV. Hence, 100 mV was chosen as the square-wave amplitude.

The potential step increment together with the frequency defines the effective scan rate. The frequency was varied in the range of 10–100 Hz and the response for carbaryl increases with frequency up to 20 Hz, above which deformation in the voltammetric shape of the carbaryl oxidation process occurred, in addition to a significant reduction in peak current.

By fixing an amplitude of 100 mV and a frequency of 20 Hz, the effect of potential step increment was studied, in the range of 1–10 mV. For potential steps greater than 2 mV, deformation of the voltammetric profile was observed and the current peak decreased in height. Hence a frequency of 20 Hz and 2 mV potential step increment were chosen, corresponding to an effective scan rate of 40 mV s^{-1}.

3.5. Analytical curve for carbaryl and recovery studies

SWV experiments were carried out in triplicate using the optimized experimental parameters to obtain an analytical curve for the determination of carbaryl with the GC/MWCNT/CoPc film electrode. The analytical curve shown in Fig. 6 has a linear response in the range of 0.33–6.61 μmol L^{-1}, according to:

$$I(\mu A\,cm^{-2}) = 0.68 \pm 0.22(\mu A\,cm^{-2}/\mu mol\,L^{-1}) + 6.71 \pm 0.09[\text{Carbaryl}](\text{mmol}\,L^{-1}) \quad (2)$$

with a correlation coefficient of 0.9991 ($n = 11$). The LOD of 5.46 ± 0.02 nmol L^{-1} (1.09 ± 0.02 μg L^{-1}) was determined using a 3σ/slope ratio, where σ is the standard deviation of the mean value for 10 voltammograms of the blank, determined according to IUPAC recommendations [27].

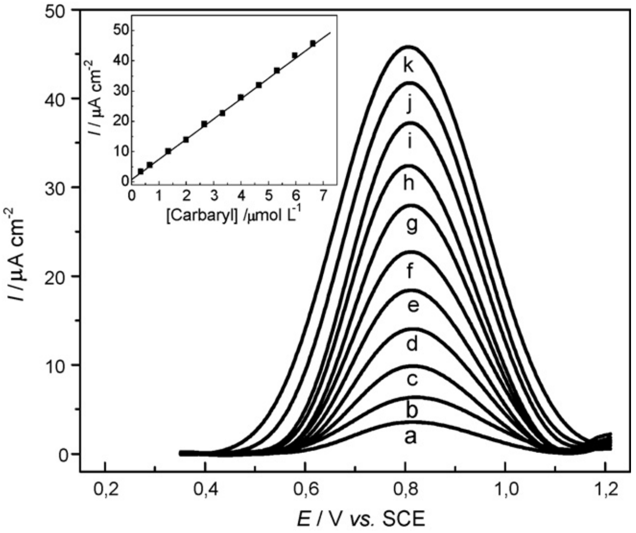


Fig. 6. Square-wave voltammograms at the GC/MWCNT/CoPc film electrode, using the optimized SW parameters; carbaryl concentrations in μmol L^{-1}: (a) 0.33, (b) 0.66, (c) 1.33, (d) 1.99, (e) 2.66, (f) 3.33 (g) 3.99, (h) 4.66, (i) 5.33, (j) 5.99 and (k) 6.62. Inset: linear dependence of peak current on carbaryl concentration.

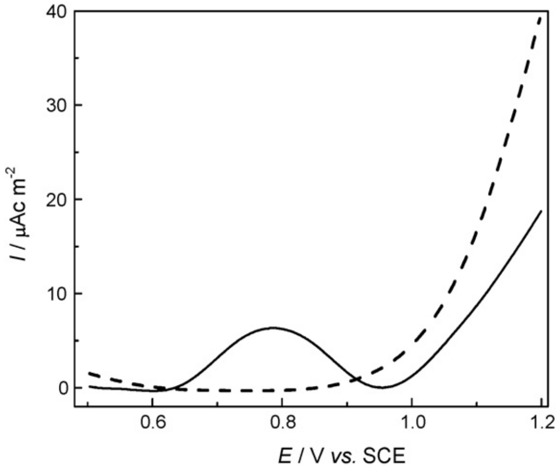


Fig. 7. Square-wave voltammograms at the GC/MWCNT/CoPc film electrode in river water in the presence (full line) and absence (dashed line) of 1.66 μmol L^{-1} of carbaryl.

The proposed method was applied to the analysis of the pesticide in river water spiked with carbaryl, using the standard addition method, in order to eliminate any matrix effects. The precision and accuracy were determined after dosing 1.66 μmol L^{-1} of carbaryl into the environmental sample solution. For this purpose, a polluted water sample with a high content of organic components was collected near Coimbra, Portugal. The SWV responses at the GC/MWCNT/CoPc electrode for river water in the presence (full line) and absence (dotted line) of 1.66 μmol L^{-1} of carbaryl are shown in Fig. 7. The percentage recoveries, obtained by the procedure described in Section 2, are given in Table 2.

Table 2
Determination of carbaryl in polluted river water sample (each value is the mean of three determinations).

	Added/μmol L^{-1}	Found/μmol L^{-1}	Recovery/%	RSD/%
Sample 1	1.66	1.53	91.9	−3.18
Sample 2	1.66	1.55	93.4	+3.27
Sample 3	1.66	1.62	97.6	+1.20

The good values observed in the recovery procedure show that the proposed method is suitable for the quantitative determination of carbaryl and that the GC/MWCNT/CoPc film electrode is efficient in the determination of carbaryl. The procedure is simple and gives limits of detection around 1.0 $\mu g\,L^{-1}$.

The method yielded values for the LOD lower than those required for environmental control for carbaryl in surface water by many government agencies, as reported by IUPAC [31]. Depending on the specific legislation, the maximum permitted residue levels in such matrices can vary from 50.0 to 1.0 $\mu g\,L^{-1}$ of carbaryl.

Comparing the results at the GC/MWCNT/CoPc film electrode with other electroanalytical methods, the direct determination of carbaryl described in [10] has a higher detection limit of 40.7 $nmol\,L^{-1}$ (8.2 $\mu g\,L^{-1}$) with analytical sensitivity of 3.07 $\mu A\,\mu mol\,L^{-1}$. For indirect detection of carbaryl following pesticide hydrolysis in alkaline medium [28,29], the detection limits found were 3.7 $\mu mol\,L^{-1}$ (74.0 $\mu g\,L^{-1}$) and 1.0 $\mu mol\,L^{-1}$ (20.1 $\mu g\,L^{-1}$) respectively. Thus a lower detection limit in SWV measurements, and higher sensitivity, were observed at the GC/MWCNT/CoPc film electrode. This can be attributed to the efficiency of the electron transfer between the modified electrode and carbaryl due to the low charge-transfer resistance of the film.

Methods that use enzymatic amperometric biosensors to detect carbaryl also showed higher detection limits of 20 $nmol\,L^{-1}$ (4.0 $\mu g\,L^{-1}$) and 50 $nmol\,L^{-1}$ (10 $\mu g\,L^{-1}$) [7,8]. Using an acetylcholinesterase (AchE) based amperometric biosensor [30], a wider linear range and lower detection limits reaching 2.98 $nmol\,L^{-1}$ (0.6 $\mu g\,L^{-1}$) was found. However, for the GC/MWCNT/CoPc film electrode, high sensitivity, good reproducibility and simple instrumentation, preparation and analytical procedure are important advantages. This method can be easily applied to the determination of other electroactive pesticides in real samples.

4. Conclusions

A new electroanalytical procedure is proposed for monitoring of carbaryl in natural waters, not requiring separations, clean-up or derivatization steps, which are indispensable in a number of other analytical methodologies. Effects of adsorption blocking of the electrode surface by the pesticide or its oxidation products are easily removed by applied potential conditioning at −0.5 V during 10 s. The electrocatalytic properties of the carbon nanotubes add to the excellent redox mediator power of the cobalt phthalocyanine to decrease the carbaryl oxidation potential compared with bare GC.

Due to the special characteristics of multi-wall carbon nanotubes and cobalt phthalocyanine as catalytic surfaces, the method yielded values for the LOD lower than those required for environmental control for carbaryl in surface waters. Finally, the application of the analytical methodology to samples prepared with contaminated water as complex matrix showed that contamination with of organic matter also hardly affects the determination. This demonstrates that the electrochemical sensor described here can be used to analyse and monitor carbaryl in real samples directly and in real time.

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