Electrochemical stripping analysis of methyl-parathion (MPT) using carbon fiber microelectrodes (CFME) modified with combinations of poly-NiTSPc and Nafion® films

Mohammed Sbãia, Hortense Essis-Tome, Ulrich Gombert, Tony Breton, Maxime Pontié

Angers University, Chemistry Department, Group Analysis and Processes (GAP), 2 Bd. Lavoisier, 49045 Angers Cedex 01, France

ENS of Abidjan, Laboratory of Applied Chemical-Physics (LACP), 08 BP 10 Abidjan 08, Ivory Coast

Received 3 December 2006; received in revised form 29 December 2006; accepted 31 December 2006
Available online 12 January 2007

Abstract

A novel carbon fiber microelectrode (CFME) was obtained by tetrasulfonated phthalocyanine (p-NiTSPc) electrodeposition on carbon surface combined with Nafion® coating for the detection of methyl-parathion (MPT). Square-wave voltammetric parameters were optimized (frequency, initial scanning potential, scan increment and pulse height). Our contribution shows the possibility of a rapid detection of MPT on a poly-NiTSPc film with a clear electrocatalytic activity towards MPT redox process. It appeared also that nickel complexes-based associated to Nafion® coating offer an indisputable advantage for developing new electrode materials in the field of electrochemical detection of the MPT and their organic derivatives.

Keywords: Methyl-parathion; Carbon fiber microelectrode; Square-wave voltammetry; Nickel phthalocyanine film; Nafion®

1. Introduction

Organophosphate (OP) compounds are significant environmental and food chain pollutants [1] because they are used intensively as pesticides, insecticides and chemical-warfare agents. Due to the high toxicity of OPs, the rapid detection of these toxic agents in the environment, public places or workplaces and the biomonitoring of individuals exposures to chemical-warfare agents become increasingly important for homeland security, health protection [2–5] due to its potential use as military or terrorists weapons [6]. MPT (O,O-dimethyl-O-(4-nitrophenyl)-phosphorothioate) is an OP insecticide very effective against many pests in important crops, such as bulbs, cereals, fruits, vegetables, cotton, peanuts, soybean, potato, sugar cane, coffee, alfalfa and pasture [7,8]. Furthermore, MPT is an inhibitor of acetylcholinesterase, therefore producing serious damage and death, also it is considered extremely toxic. Analyzing MPT in environmental and biological samples is routinely carried out using analytical techniques, such as gas or liquid chromatography and mass spectrometry [9,10]. Such analysis is generally performed at centralized laboratories, requiring extensive labor and analytical resources, and often results in a lengthy turn-around time. In order to give appropriate results within a short time under field conditions or on-line monitoring, various inhibition and non-inhibition biosensor systems, based on the immobilization of acetylcholinesterase or organophosphorus hydrolase onto various electrochemical or optical transducers, have been proposed for field screening of OP neurotoxins [11–18]. Specific antibodies against OP pesticides have been recently developed for enzyme-linked immunoassay [19]. Amperometric electrochemical detection of OPs was developed by applying constant potential in connection with high-performance liquid chromatography [20] or capillary electrophoresis [21]. Martinez et al. [20] developed an automated high-performance liquid chromatographic method for the
Optimizing the square-wave voltammetric (SWV) parameters (frequency, initial scanning potential, scan increment and pulse height) for a more sensitive detection of the MPT.

2. Experimental

2.1. Apparatus and carbon microelectrode (CME)

Cyclic voltammetric (CV) and square-wave voltammetry measurements were performed using an electrochemical analyzer PG580 (Princeton Applied Research, PCR, USA) connected to a personal computer. A three-electrode configuration was employed, consisting of a carbon microelectrode (12 μm diameter and 50 μm length, see Fig. 1) serving as a working electrode and purchased by Radiometer Analytical (carbon fiber electrode MFC1, no. 11101405 serie 2). The carbon electrode surface was renewed by a homemade electrochemical treatment detailed below. The potentials are expressed with reference to the aqueous saturated calomel electrode (SCE). This reference electrode was purchased by Radiometer Analytical (type XR100, standardization certificate no. XG2004-415, serie no. 129-15-012) and a platinum wire served as the counter electrode. Ten CFME were tested and six were sufficiently sensitive to permit a complete study. Electrochemical experiments were carried out in a 10-mL glass voltammetric cell at room temperature (20°C).

2.2. Reagents

Methyl-parathion was purchased from Sigma–Aldrich, and their 10.000 mg L⁻¹ stock solutions were prepared in acetonitrile. A 0.2 M of acetate buffer (pH 5.2) was used as the supporting electrolyte. In this buffer, the MPT solutions concentra-
The concentration range was prepared between 0.01 and 50 mg L\(^{-1}\), NiTSPc (batch 20526KA) and Nafion\(^{\circledast}\) (see Fig. 2) were purchased from the Aldrich and used as received. Deionized water was obtained from a Elga Labwater ultrapure-water system (Purelab-UVF, Elga, France).

2.3. Procedure

A carbon fiber microelectrode was immersed into a stirring acetate buffer containing the desired concentration of MPT in the 10 ml electrochemical cell. SWV scanning was performed from \(-1.1\) to +0.3 V with a step potential of 10 mV, amplitude of 60 mV and a frequency of 60 Hz, the optimized conditions obtained (see Section 3).

The carbon microfiber electrodes were first electrochemically pre-treated in a mixture of H\(_2\)SO\(_4\) (0.5 M)/ethanol (pure solution) (50/50, w/w) under the following conditions: cyclic voltammetry in 0.2 M acetate buffer (pH 5.2), potential scanning rate: 100 mV s\(^{-1}\) in the potential range \([-1.0; +1.5 \text{V/SCE}]\) during 20 cycles. After one or two pre-treatments MPT redox couples appeared (see Fig. 3) showing the well activation of the CFME. A pair of rather well defined redox peaks (E\(_{pa}\), 0.06 V and E\(_{pc}\), 0.0 V) and irreversible reduction peak (E\(_{pc}\), \(-0.61 \text{V}\)) were observed in the potential range from \(-1.0\) to \(1.0 \text{V}\).

Electrochemical treatment of pyrolytic carbon fiber electrodes is usually recommended by the suppliers in order to increase the sensitivity and selectivity performances of the fibers, specially for in vivo studies [38]. In the present study, the total absence of peak in presence of MPT were observed first with the commercialize CFME. The idea of the activation using H\(_2\)SO\(_4\)/EtOH solution is only empirically justified. But much more work is needed to support a valuable hypothesis about the mechanism by which such treatment act.

During the experiments with pre-treated unmodified CFME, we observed the adsorption of the MPT or its by-products (see Fig. 4). We can hypothesis the presence of the \(p\)-nitrophenol as a well-known MPT metabolite to explain the large peak width observed at 0.0 V of Fig. 4 in comparison with Fig. 3. Then we decided to engage the protocol described below for renewing periodically the CFME surface after its contact with MPT. This electrochemical cleaning treatment shows satisfactory results, as illustrated in Fig. 4. But as usually admitted the repetition of electrochemical cycling to carbon electrode is carbon consumer and the consequences on the electrodes sensitivity could be dramatic. Then we decided to follow the fiber surface with optical analysis (see Fig. 1) in order to better estimate the modifications of the CFME length during those electrochemical cleaning treatments.
The electrochemically pre-treated CFME were coated by a poly-NiTSPc electrodeposited film. The electrochemical deposition of poly-NiTSPc film was achieved in 0.1 mol L$^{-1}$ NaOH + 2 mmol L$^{-1}$ NiTSPc aqueous solution by repeated potential scans (50 times) between 0.2 and 1.3 V/SCE (scan rate: 100 mV s$^{-1}$), as previously detailed [36,39]. A typical example of the cyclic voltammograms deposition of a p-NiTSPc film is shown in Fig. 5.

The nickel-based complex film thickness can be estimated by taking into account the calculation of the electrode surface coverage, based on the charge under the oxidative peaks observed at 0.4 V/SCE, and the shape and size of the phthalocyanine macrocycle, as previously detailed [36,39]. The apparent surface coverage of the film by nickel phthalocyanine should be evaluated from the last cyclic voltammogram. In our considered case, NiTSPc-based films were prepared either by 50 potential scans. This leads to the deposition of $2 \times 10^{-9}$ mol cm$^{-2}$. This corresponds approximately to 30 nm. It is important to note that the reproducibility of the NiTSPc deposition is maximal if the CFMEs were electrochemically pre-treated. Thus, it clearly appears that very thin NiTSPc films can be easily obtained by cyclic potential scans, and that the film thickness can be controlled by the number of potential scans.

Further coverage of the CFME with Nafion$^\circledR$ was obtained by two sequential dipping (during 30 s each time) in 5% aqueous-alcohols solution of Nafion$^\circledR$ and drying in an oven at 60 °C for 50 min.

Fig. 6 shows a typical SWV voltammogram of MPT in 0.2 M acetate buffer (pH 5.2). A very sharp and well-defined peak was obtained at the potential range from −1.1 to 0.3 V. The peak potential of the oxidation peak was 0.08 V.

In order to obtain a more sensitive detection of the MPT the following square-wave voltammetric parameters: frequency, initial scanning potential, scan increment and pulse height were optimized.

These profiles are consistent with those described elsewhere [8,19,23] for OP pesticides and nitroaromatic compounds. Before MPT experiments a control experiment was performed under the same conditions in the absence of methyl-parathion (see baseline Fig. 4) and no redox peak was observed.

3.2. Square-wave voltammetry optimization

Fig. 6 shows a typical SWV voltammogram of MPT in 0.2 M acetate buffer (pH 5.2). A very sharp and well-defined peak was obtained at the potential range from −1.1 to 0.3 V. The peak potential of the oxidation peak was 0.08 V.

In order to obtain a more sensitive detection of the MPT the following square-wave voltammetric parameters: frequency, initial scanning potential, scan increment and pulse height were optimized.
Fig. 7. Variation of oxidation peak intensity vs. initial scanning potential (a), frequency (b), scan increment (c) and pulse height (d) (in 0.2 M acetate buffer pH 5.2, [MPT] = 50 mg L$^{-1}$).

Fig. 7(a) shows the variation of the intensity of oxidation peak with the initial scanning potential between $-1.4$ and $-0.1$ V. The obtained results confirm that no stripping peak can be observed when the initial potential is higher than $-0.5$ V. Oxidation peak reaches a maximum of the current at $-1.1$ V which was adopted for all the following experiments.

Fig. 7(b) presents the frequency variations influence upon the SWV response in terms of stripping peak current. First, the peak current increases with the increase of the SWV frequency and then is stabilized to a level of 60 Hz. This value was adopted for all the following experiments.

The variations of peak current with the scan increment is shown in Fig. 7(c). As can be observed, no stripping peak current appeared before 5 mV. Beyond this point, the peak current increases rapidly with the increase of the scan increment up to 10 mV and then reaches a constant stage. The same behavior was obtained in the case of the variation with pulse height (Fig. 7(d)). The response in term of peak current increases slightly with the increase of the pulse height at first and then goes off to reach the upper limit of 60 mV.

Thus, all SWV experiments in this work were performed using a frequency of 60 Hz, a scan increment of 10 mV, a pulse height of 60 mV and a scanning potential range from $-1.1$ to 0.3 V.

3.3. Performances of unmodified and modified CFMEs

Fig. 8 shows the SWV voltammograms of MPT at unmodified and C/p-NiTSPc, C/p-NiTSPc/Nafion® modified CFMEs. One remarkable result can be emphasized from these data, the electropolymerized p-NiTSPc coating shows a clear electrocatalytic activity towards MPT redox process.

Fig. 9 shows that an irreversible passivation of the electrodes appeared for MPT concentrations higher than 10 mg L$^{-1}$ specially for the C, C/p-NiTSPc, C/Nafion®/p-NiTSPc and C/Nafion® CFMEs, suggesting that the oxidation products of this compound alter the nickel-based film redox and also the carbon properties. Such a passivation phenomenon was also observed in the case of the phenol oxidation. $p$-Nitrophenol was also investigated, and it appeared that the nickel complexes-based was able to suppress electrode passivation during the anodic oxidation of the phenols [40]. In the case of C/p-NiTSPc/Nafion® composite multilayer no passivation was observed (Fig. 9(a)). We can hypothesis the increase in the
MPT adsorption sites number due to the Nafion® coating in comparison to the p-NiTSPc film alone (Table 1).

Under 10 mg L\(^{-1}\), Fig. 9 shows not any apparent passivation of the electrodes, the higher sensitivity calculated was obtained for the modified C/Nafion®/p-NiTSPc CFME. Furthermore, in the case of passivation the MPT and their by-products (i.e. p-nitrophenol) deposited were easily eliminated by the electrochemical cleaning described in Fig. 4 for the illustration of a reversible adsorption under CFME.

The gain in term of sensitivity for the p-NiTSPc modified CFME is non-negligible and the limit of detection was 0.1 mg L\(^{-1}\) in comparison to 1 mg L\(^{-1}\) obtained for the unmodified carbon fiber. The effect of scan rate on the electron transfer rate for methylparathion at the C/p-NiTSPc film electrode were studied by cyclic voltammetry (CV). The results from CV showed that \(I_{\text{peak}}\) varies with the root of the scan rate \(I_{\text{peak}} = 9v^{1/2} - 94R^2 = 0.98\). Then the peaks currents were proportional to \(v^{1/2}\), as expected for a diffusion-controlled charge transfer at the electrode surface [41]. Furthermore, the ratio \(I_{\text{peak}}\) (anodic)/\(I_{\text{peak}}\) (cathodic) is constant with the scan rate and the value is 0.92. \(\Delta E_p\) for the modified CFME stays constant to the value of 30 mV which suggests that two electrons participate in the oxidation of \(\Phi_1\)-NHOH conformly to reaction (2). Then reported data indicated that the presence of p-NiTSPc film increases the electronic transfer rate for the redox couple \(\Phi_1\)-NHOH/\(\Phi_1\)-NO in comparison to the unmodified carbon electrode from an irreversible system to a reversible.

Similarly, Goux et al. [42] found that Ni tetra-aminophthalocyanine films electrodeposited in dimethylformamide increase their activity for dopamine electro-oxidation having been cycled in aqueous alkaline solution, a process which was suggested to be attributed to interconnected O–Ni–O oxo bridges. Recently, Zagal et al. reported on poly-NiTSPc/ITO electrodes and showed by UV–vis spectroscopy that poly-NiTSPc retains the original phthalocyanine structure and by XPS that Ni in the film had an environment very similar to that in nickel hydroxide, in agreement with a hydroxi-oxo structure for the p-NiTSPc films. In addition, p-NiTSPc films on gold electrode show a moderately non-Nernstian behavior with a peak separation of 120 mV at a scan rate of 0.01 V s\(^{-1}\). This moderate irreversibility is in agreement with the modest value of the activation energy of Ni(II) electro-oxidation, 38 kJ mol\(^{-1}\). Therefore, both the electron transfer between the Au electrode and the NiTSPc film, and the electron transfer between Ni atoms, must be fairly rapid. And for sufficiently thick films the kinetics of the Ni(III)/Ni(II) process is the typical one for diffusion control in a semi-infinite medium, the electrodeposited film. Finally, the authors reported that p-NiTSPc film elaborated and cycling in NaOH is in the form of \(\Phi_1\)-Ni(OH)\(_2\) very similar to that in nickel hydroxide [37].

To compare the performances of the different modified CFMEs elaborated, C/p-NiTSPc, C/Nafion®, C/Nafion®/NiTSPc, C/p-NiTSPc/Nafion®, we defined the parameter \(G\) as:

\[
G = \left( \frac{I_{\text{peak modified}}}{I_{\text{peak unmodified}}} - 1 \right) 100
\]

with \(I_{\text{peak modified}}\) the maximum intensity obtained in the optimum SWV conditions for the different coatings and \(I_{\text{peak unmodified}}\).
of Nafion® as an outer membrane coating decrease dramatically. Ods have a number of disadvantages, limiting their applications primarily to laboratory settings and prohibiting their use for rapid analyses under field conditions. To meet these requirements of rapid warning and field deployment, more compact low-cost instruments, coupled to smaller sensing probes, are highly desirable for facilitating the task of on-site monitoring of OP compounds for portable experiments.

Acknowledgement

The authors would like to thank Mrs. Claire Compion (PaVé, INRA-Univ. d’Angers) for her useful assistance to carry out the optical analysis of the microelectrodes.

References

Biographies

Mohammed Sbaï born in July 28, 1974, in Fès, Morocco. He has a PhD diploma in physical-chemistry from the University of Franche-Comté, Besançon, France. He prepared his DSc degree under the direction of professors Fievet and Szymczyk and finished it in November 2004. He received a research award for his work dedicated to the determination of electrokinetic potential of porous membranes by the “Club Français des Membranes” last November. He occupied during 2 years a temporary function of assistant lecturer at the Universities of Tours and Angers, France. His research interests were characterization of electrokinetic properties of separators used in the fabrication of the Li-ion batteries and detection of organic pollution in the environment matrices using carbon fibers ultramicroelectrodes. Currently, he is preparing his diploma of the second year of professional master of innovation in agro-alimentary at Institute of Sciences and Technologies of Engineers of Angers (ISTIA), France.

Hortense Essis-Tôme born in 1961 in Abidjan, Ivory Coast. She is assistant-professor at the ENS of Abidjan, in the Ivory Coast. She is the head director of the Chemistry Department. She is just starting a new laboratory dedicated to organics pollutants treatment and analysis in environmental matrices.

Ulrich Gombert born in 1983, is a MSc student of the University of Angers, France. He is currently following the courses of the master sciences and engineering of the environment in the Chemistry and Environment Department of Angers University, France.

Tony Breton born on August 11, 1977, in La Rochelle, France, is assistant-professor and works at the University of Angers, France. He is a member of the Group Analysis and Processes. He received a DSc degree of electrochemistry under the direction of professors Jean-Michel Léger and Mustapha Belgsir in 2004 from the University of Poitiers, France. After a 1 year postdoctoral research study on the electrochemical modification of electrode with professor Daniel Bélanger, Montreal, Canada, his current work concerns the covalent functionalization of carbon electrode for electrochemical sensors dedicated to environmental analysis.

Maxime Pontié born on March 14, 1968, in Montauban, France, is professor and works at the University of Angers. He is the head director of the Group Analysis and Processes, Angers, France. He received a DSc degree under professors Lemordant and Rumeau in 1996 from the University of Francois Rabelais in Tours, France. After a postdoctoral research study on streaming potential measurements in nanofiltration with professor Bowen, Swansea University, Wales, UK, his current research interests is new molecular materials as polymer-based complexes and nanocomposite materials for their application in analytical chemistry specially for amperometric sensors conception dedicated to environmental and biological matrices.