

Full Paper

Sensitive and Selective Electrochemical Analysis of Methyl-parathion (MPT) and 4-Nitrophenol (PNP) by a New Type p-NiTSPc/p-PPD Coated Carbon Fiber Microelectrode (CFME)

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Abstract

A novel modified carbon fiber microelectrode (CFME) was obtained by combination of tetrasulfonated nickel phthalocyanine (p-NiTSPc) electroformed film associated to *para*-phenylenediamine (p-PPD) electropolymerized outer-coating. The modified CFMEs were denoted C/p-NiTSPc and C/p-NiTSPc/p-PPD, respectively. These electrodes are dedicated to the organophosphates compounds (OPs) methyl-parathion (MPT) and *para*-nitrophenol (PNP). Our contribution shows that both OPs can be determined simultaneously on the unmodified and modified C/p-NiTSPc CFMEs. A clear electrocatalytic activity towards both MPT and PNP redox process was observed, for the first time, in presence of p-NiTSPc. The obtained sensitivity for the C/p-NiTSPc CFME was 80 nA L mg⁻¹ in the concentration range 0.01 to 10 mg/L with a detection limit of 40 µg/L. Also the combination of p-NiTSPc and p-PPD electrodeposited films show, for the first time, the possibility to discriminate on the C/p-NiTSPc/p-PPD CFME between MPT and PNP. Stability experiments were also conducted for 3 weeks in acetate buffer showing a good reproductibility of the sensitivity to PNP vs. time in presence of MPT with a little loss of sensitivity (5%) after 3 weeks.

Keywords: Methylparathion, *para*-Nitrophenol, Carbon fiber microelectrode, Nickel-phthalocyanine, *para*-Phenylenediamine, Sensitivity, Selectivity, Durability

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1. Introduction

Organophosphate compounds (OPs) and their metabolites are significant environmental and food chain pollutants because they are used intensively as insecticides and chemical-warfare agents [1]. 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 is an inhibitor of acetylcholinesterase [7–12] and PNP, its main hydrolysis by-product, is itself responsible for methemoglobinemia. The maximum limits for drinking water permitted by the European Commission is 0.1 µg/L, the Brazilian Environmental Council fixed a value of 100 µg/L and the EPA (USA) has established a Lifetime Health Advisory (LHA) level of 60 µg/L for PNP in drinking water. MPT is rapidly metabolized by both plants and animals but it could also be bioconcentrate due to its high K_{oc} and $\log K_{ow}$ (see Table 1). But in most situations, MPT adsorbs to soil particles and degrades rapidly. On the contrary 4-nitrophenol biodegrad-

ability in environment is not very good due to its low values of the parameters K_{oc} and $\log K_{ow}$ (see Table 1). Bioaccumulation of this compound is considered to rarely occur [13, 14]. It has been detected in the treated effluents of the following industries : electrical/electronic components (< 22 µg/L mean, 35 µg/L max organic chemicals) manufacturing/plastics (190 µg/L max). Additionally the raw wastewater of the following industries contained PNP: auto and other laundries (14 µg/L mean), aluminum forming (18 µg/L max), metal finishing (10 µg/L max) and photographic equipment/supplies (57 µg/L max) [15].

Analyzing OPs in environmental and biological samples is routinely carried out using analytical techniques such as gas or liquid chromatography and mass spectrometry [16, 17]. 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 organophosphorous hydrolyase onto various electrochemical or optical transducers, have been proposed for field screening of OP neurotoxins

Table 1. Properties of the studied MPT and PNP organophosphorous. (PNP has a pKa of 7.08 at 22 °C).

Compounds' properties	MPT	PNP
MW (g/mol)	263.23	139.11
Solubility 20° (C mg/L)	55	11 600
log K_{ow}	> 4.1	1.9
K_{oc} (mg/L)	1500	> 200
Half life	1–60 days	1–3 years
Water and effluent contents encountered	few ng/L	0.01–190 µg/L

[18–33]. Amperometric detection of OP nerve agents was also developed by Wang et al. [34].

1.1. Direct or Indirect Electrochemical Detection of OPs

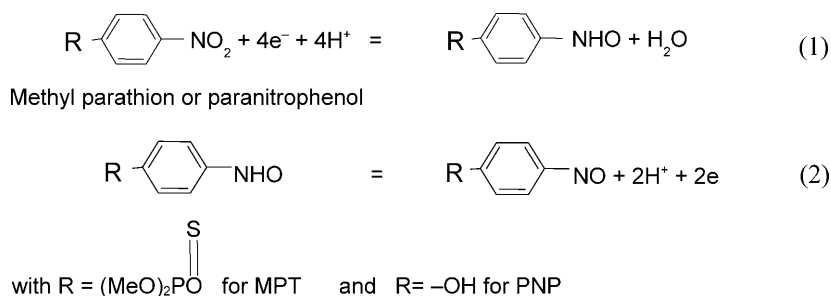
Usually on carbon electrode a pair of rather well defined redox peaks (E_{pa} , 0.08 V and E_{pc} , 0.0 V) and irreversible reduction peak (E_{pc} , -0.61 V) were observed in the potential range from -1.0 to 1.0 V. The irreversible reduction peak of OPs corresponds to the reduction of the nitro group to hydroxylamine (Reaction 1) and the reversible redox peaks are attributed to two-electron-transfer process (Reaction 2).

These results are consistent with those described elsewhere [27–29, 35, 36] for OPs and nitroaromatic compounds. Before MPT experiments a control experiment was performed under the same conditions in the absence of MPT and no redox peak was observed, as recently reported [28].

Then two possibilities are usable for OPs detection: direct reduction under cathodic potential, as recently reported [37] with a determination limit at 1.2 µg/L. Several applications and electroanalytical methodologies employing micro-electrodes as working electrodes for indirect quantification via the hydroxylamine adsorbed product of OPs were recently reported using TiO₂ and gold nanoparticles and nanotubes [36, 38–41].

A recent review reported the different approaches that have been taken in the development of electrochemical modified sensors incorporating carbon as the principal electrode substrate [42]. A preliminary work, recently reported [43], indicated that the best responses, considering the intensities of the current and voltammetric profile for the paraquat reduction process, were obtained when the

electrode modified by cobalt phthalocyanine was employed, which had a better catalytic activity as a result of this modification compared with that for an unmodified electrode and electrodes modified by iron, manganese and the acid form of the phthalocyanines. The authors showed a linear relation, with detection and quantification limits of 26.53 and 88.23 µg/L. Further recently hanging mercury drop electrode associates with differential pulse stripping voltammetry was applied to several vegetable samples for pesticide compounds in a mixture of MPT, fenitrothion and parathion. But to limit mercury use porous graphite detector were developed [35, 44]. In [45] the authors have demonstrated the feasibility of using HPLC with electrochemical detection (ED) to separate and detect a variety of organo-nitro pesticides and their toxic degradation byproducts (i.e. PNP). Liu et al. [35] proposed a sensitive electrochemical stripping voltammetric method for analyzing OPs using a carbon paste electrochemical transducer with a limit of detection of 12.5 µg/L and a preelectrolysis time of 10 min. Recently Sbai et al. [28] proposed, for the first time and without preelectrolysis time, a novel carbon fiber micro-electrode modified with combinations of nickel phthalocyanine and Nafion for the detection of MPT with a sensitivity of 20 nA L mg⁻¹ and a determination limit of 100 µg/L under optimized square-wave voltammetry (SWV) parameters. Hernandez et al. [44] used a C₁₈-modified carbon paste glassy carbon electrode for the determination of MPT with a detection limit of 7.9 µg/L. Furthermore the same authors show for the first time that a IIs-based modified electrodes was able to permit the simultaneous determination of both MPT and PNP [37]. The determination of both MPT and PNP and three others OPs has been studied for the first time by differential pulse voltammetry with a carbon-paste electrode modified with 50% (w/w) of C₁₈. A study of the influence of the pH in the preconcentration cell and the measurement cell was carried out for an electrode with 50% modifier and an accumulation time of 5 min. The voltammograms were recorded with a sweep rate of 40 mV s⁻¹ and a pulse amplitude of 50 mV. With the optimum conditions of pH for both of the steps, various other variables were studied. The variables for each compound were optimized and the possibility of application to the determination of a mixture of the four compounds was investigated. The determination limits found for both compounds are 4.3 µg/L and 7.9 µg/L for PNP and MPT, respectively. The method was applied to samples of a small lake which gathers rain



Scheme 1.

water and water filtered from land on which cereals are grown [37]. Very recently Fan et al. [36] proposed an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate-single-walled carbon nanotube paste coated glassy carbon electrode with a limit of detection of 250 $\mu\text{g/L}$. An elegant method of microelectrode modification for pesticides detection is the electropolymerization of suitable monomers such as nickel porphyrin or nickel phthalocyanine, as reported elsewhere [26, 28, 32, 42, 43, 46–48]. The major additional advantages of such modification design is its ability to coat very small or irregularly shaped surfaces. It is important to mention that the current efficiency of the porphyrinic or phthalocyanine modified microelectrodes depend significantly on the quality of the polymeric film, the purity of the starting monomers, the potential range of electroformation and others experimental parameters [47]. Progress in this area is also strongly connected to the design of new neutral polymeric electroformed films which possess high potentialities usable in order to increase sensors selectivity and sustainability. The interest in phenyldiamine electropolymerized films is strongly connected to the design of new electroactive polymeric systems and to the success in forming thin, insoluble, stable, reproducible and adherent films on electrode surfaces. It permits also to modulate the nanoporosity of the outer membrane deposited which is dependant under few parameters [48–51].

We report here, for the first time, the use of nickel(II) tetrasulfonated phthalocyanine (p-NiTSPc) associated to *para*-phenyldiamine (p-PPD) coating as a molecular coating elaborated to develop a new sensor (denoted C/p-NiTSPc/p-PPD) dedicated to better sensitive and selective determination of PNP in presence of MPT, in comparison to unmodified carbon fiber microelectrode.

In order to achieve our goals, this study was conducted by:

- comparing the sensitivity to MPT and PNP for unmodified and modified by C/p-NiTSPc CFME under optimized SWV operating conditions;
- improving the selectivity of PNP determination in presence of MPT and PNP by integration of a p-NiTSPc mediator film with an electropolymerized p-PPD neutral film coating;
- studying the stability of the new CFME C/p-NiTSPc/p-PPD vs. time (for three weeks).

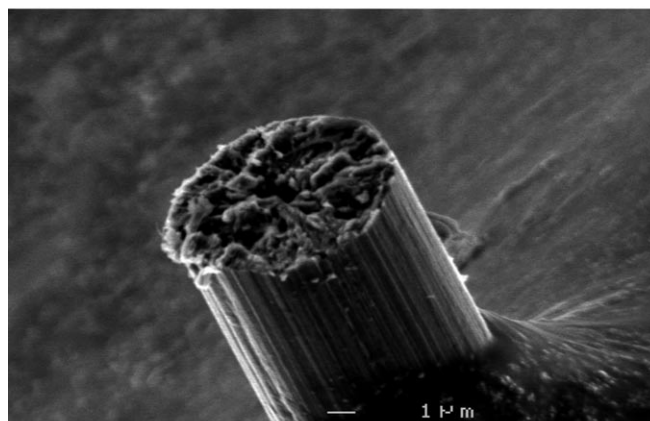
2. Experimental

2.1. Apparatus and Unmodified Carbon Fiber Microelectrodes (CFME)

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) 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, see Fig. 1) and 1 mm length, serving as a working electrode purchased by Group Analysis and Processes (GA&P) (Angers University,



a)



b)

Fig. 1. a) Photography of the homemade modified C/p-NiTSPc CFME GA&P made in Angers, France. b) 2D SEM image of the unmodified CFME.

France). Electrochemical experiments were carried out in a 10-mL glass voltammetric cell at room temperature (20 °C). The carbon electrode surface was renewed by a homemade electrochemical treatment detailed in a previously work [28]. 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 n°XG2004-415, series n°129-15-012) and a platinum wire served as the counter electrode. In order to estimate the performances of all the microsensors (10 CFME were elaborated) a quality control of the carbon fiber cleanness with optical tests and electrochemical tests with probes $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{NH}_3)_3^{3+}$ (results not shown). For 10 homemade CFMEs (see Fig. 1a) tested, 6 were sufficiently sensitive after the quality control to permit a complete study. Concerning their reproducibility unfortunately we can not guarantee the

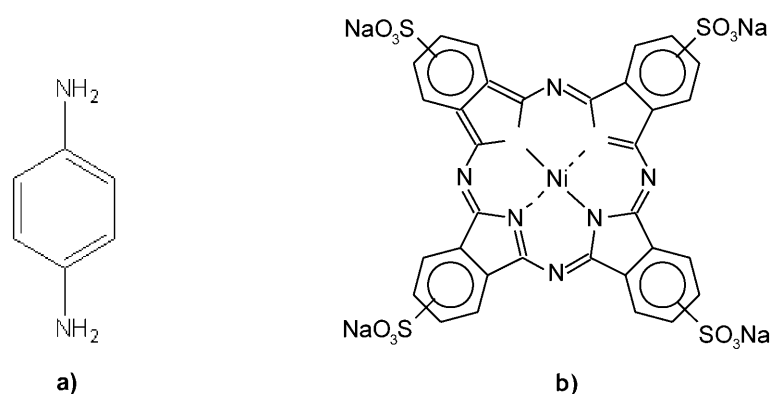


Fig. 2. Chemical structures of the monomers: a) phenylenediamine (PPD) and b) Nickel tetrasulfonated phthalocyanine (NiTSPc).

perfect similarity of each CFME due to the fact that each CFME is unique. Then on the six electrodes kept for the present study we estimated, considering sensitivity and determination limit parameters, a deviation from the norm/mean at 10%.

2.2. Reagents

MPT was purchased from Sigma-Aldrich, and their 10.000 mg L⁻¹ stock solutions were prepared in acetonitrile and PNP from Fluka as a powder with analytical grade. A 0.2 mol/L of acetate buffer (pH 5.2) was used as the supporting electrolyte. MPT and PNP acetate buffer solutions were prepared in a concentration range between 0.01 to 10 mg L⁻¹. PPD (*para*-phenylenediamine dihydrochloride) (see Fig. 2a) and NiTSPc (see Fig. 2b) (batch n°20526KA) monomers were purchased by Sigma 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 acetate buffer solution containing the desired concentration of OPs (MPT and/or PNP) in the 10 mL electrochemical cell. A typical cyclic voltammogram of a MPT solution in acetate buffer is reported in the Figure 3. Square-wave voltammetry (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, under the optimized conditions determined recently by Sbaï et al. [28].

The carbon microfiber electrodes were first electrochemically pretreated in a mixture of H₂SO₄ (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 to 1.5 V/SCE during 20 cycles.

During the experiments with pretreated unmodified CFME we observed the adsorption of the MPT and its by-

products and decided to engage the protocol described below for renewing periodically the CFME surface. This electrochemical cleaning treatment shows satisfactory results, as recently reported [28].

The electrochemically pretreated CFME were first 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). A typical example of the cyclic voltammograms deposition of a p-NiTSPc film on a CFME is shown in Figure 4. The apparent surface coverage of the film by nickel phthalocyanine should be evaluated from the last cyclic voltammogram. It is also important to notify that the reproducibility of the p-NiTSPc film deposition is maximal if the CFME is electrochemically pretreated. Thus, it clearly appears that very thin p-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 p-PPD was achieved in 5 mmol L⁻¹ PPD deaerated acetate buffer solution (pH 5.2 and ionic strength 0.2 mol L⁻¹) by repeated potential scans (10 to 20 times) between 0 and 1.2 V/SCE (scan rate: 100 mV s⁻¹), as previously detailed [46, 51].

2.4. AFM Experiments

The AFM (atomic force microscopy) equipments used were conducted with a Nanoscope III device from VEECO (USA). The membrane morphologies were imaged in contact mode in air with a scan rate of 1 Hz and 400·400 pixel resolution. The cantilevers used for such imaging were from Veeco (Dourdan, France), with a specified spring constant between 0.44–0.63 nN and a resonant frequency of 17–20 kHz. The mean roughness (denoted *R_a*) is the mean value of surface relative to the centre plane. The plane for which the volume enclosed by the image above and below this plane are equal and is calculated as

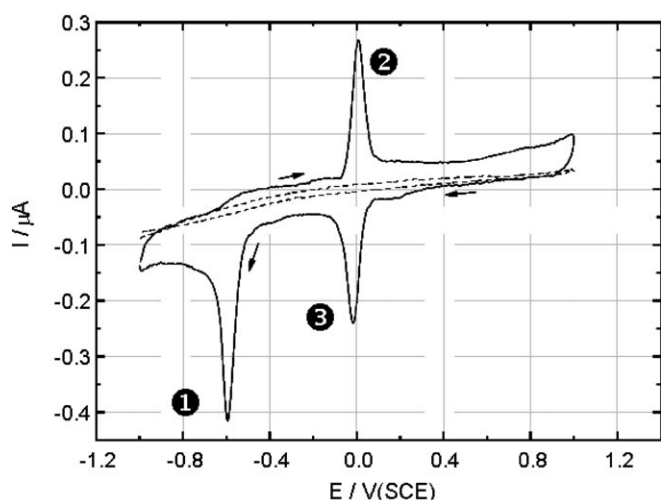


Fig. 3. Cyclic voltammograms of MPT on CFME, root line is the baseline, dotted line the CFME signal in 0.2 M acetate buffer pH 5.2. Potential scanning rate: 100 mV s^{-1} . Methyl parathion concentration 40 mg L^{-1}

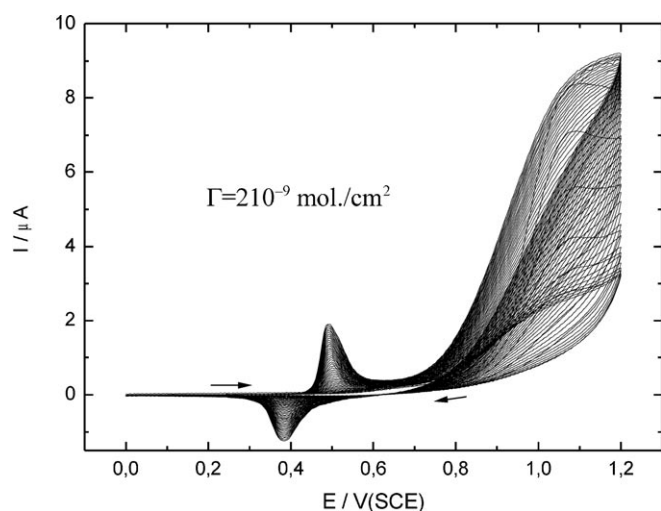


Fig. 4. 50 successive cyclic voltammograms of CFME in a 0.1 mol L^{-1} NaOH aqueous solution + 2 mmol L^{-1} of NiTSPc; electrode area = 0.075 mm^2 , potential scan rate = 0.1 V s^{-1} .

$$Ra = \frac{1}{LxLy} \int \int [f(x, \bar{a}y)] dx dy \quad (3)$$

where $z(x,y)$ is the surface relative to the center plane and Lx and Ly are the dimensions of the surface analyzed. The roughness parameter depends on the curvature and size of TM-AFM tip, as well as on the treatment of the captured. Therefore, the roughness parameter should not be considered as absolute roughness values. However the same cantilever was used for all AFM images and all the AFM treated in this way. The sensor surface samples were primarily washed and wetted with pure water and dried at room temperature in a desiccator. The samples were then

attached to steel discs with double side-scotch tape. The images were obtained over a small area of $2 \times 2 \mu\text{m}^2$.

Image analysis was carried out by means of (SPMLab602) software from VEECO France, licensed for GA&P. The surface analysis software associated with the explorer can give full details about features of the surface such as peak to valley ratio, average roughness and root mean square roughness. We focalized our attention to Ra values for unmodified and modified C/p-NiTSPc and C/p-NiTSPc/p-PPD CFMEs. In the present study Ra values are resulting from 2 fields analysis on each samples using two analysis mode, contact and tapping (images not shown). But we decided to report presently only 3D-images obtained in contact mode. For Ra , the values reported are the means average values of 2 fields analyzed (size $2 \times 2 \mu\text{m}^2$) for each mode (contact and tapping).

2.5. FESEM Analysis

Unmodified pretreated CFME were observed by FESEM (field emission gun scanning electron microscopy) analysis for a morphological study of the carbon fiber surface (see Fig. 1b). The apparatus used was JSM-6301F from JEOL (SCIAM, Angers university). Images obtained were from secondary electrons under 3–5 keV with magnifications situated between 3000 and 5000. Carbon fibers were dessicated and glued to a carbon support (see Fig. 1b). Finally thin film carbon of 2 nm thickness was deposited by evaporation under vacuum (BAL-TEC MED 020 Balzers Lichtenstein apparatus).

3. Results and Discussion

3.1. Improving Sensitivity and Selectivity for the Unmodified and p-NiTSPc Modified CFMEs

Figure 5 shows a typical SWV voltammogram of unmodified and modified C/p-NiTSPc CFMEs for a solution containing MPT and PNP under 10 mg/L in 0.1 M acetate buffer pH 5.2. Narrow peaks were obtained for the unmodified CFMEs. Very sharp and well defined peaks were obtained for the C/p-NiTSPc modified CFME with a current intensity 4 times higher in presence of p-NiTSPc. The peaks potentials are 0.0 V/SCE and 0.2 V/SCE for MPT and PNP, respectively.

Usually electrocatalysis is characterized by shift of oxidation potential to a less positive value or reduction potential to a less negative value and enhancement of cathodic or anodic current or both. In this work, the film p-NiTSPc enhances electronic communication between OPs and the electrode surface, thus displaying electrocatalytic effect. There is no significant shift in potential for Equation 2. However there is a significant increase in currents for both OPs with a 4 times increase currents. In order to definitively associate the peak intensity growth to a catalytic effect, we determined the roughness of unmodified and the modified

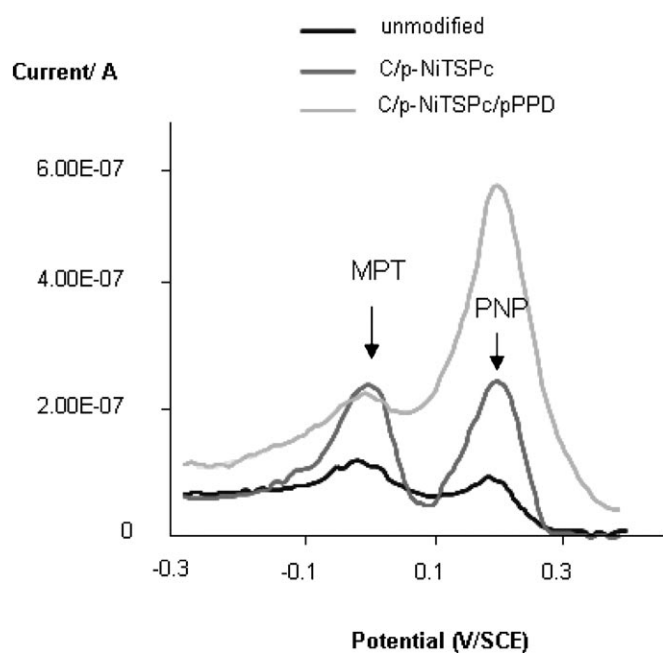


Fig. 5. SWV voltammograms of unmodified, C/p-NiTSPc and C/p-NiTSPc/p-PPD CFMEs in presence of MPT and PNP in 0.2 M acetate buffer pH 5.2, [MPT] = 10 mg L⁻¹, [PNP] = 10 mg L⁻¹; initial potential = -1.1 V/SCE, frequency = 60 Hz; Scan increment = 10 mV; Pulse height = 60 mV.

C/p-NiTSPc CFMEs surfaces by AFM. Average roughness values are reported in Table 2 (see Fig. 6). As can be observed *Ra* values decreased after p-NiTSPc deposition from 80 nm to 47 nm. This decrease can be correlated to the thickness of the p-NiTSPc film deposited with a smoothing effect.

Indeed, 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. one can imagine that the oxidation of OH during the first oxidative potential scan at $E = 0.8$ V, creates a variety of functional groups on the electrode surface leading to the coupling of the NiTSPc complexes to the electrode surface via an -O-Ni(II) bond. During the further scans i.e., further oxidation at $E = 0.8$ V, the attached Ni(II) complexes undergo oxidation to Ni(III) and bind to a new coming Ni-complex, supplied to the electrode surface by diffusion, via oxo-bridges. Thus, the film structure is imposed by the stacking of the complex layers via the interconnecting oxo-bridges, and does not depend on the electrochemical deposition procedure (cyclic voltammetry or controlled potential electrolysis). 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 or reductive peaks observed at 0.4 V/SCE, and the shape and size of the phthalocyanine macrocycle, as explained in [52]. In our considered case, p-NiTSPc-based films were prepared either by 50 potential scans. This leads to the

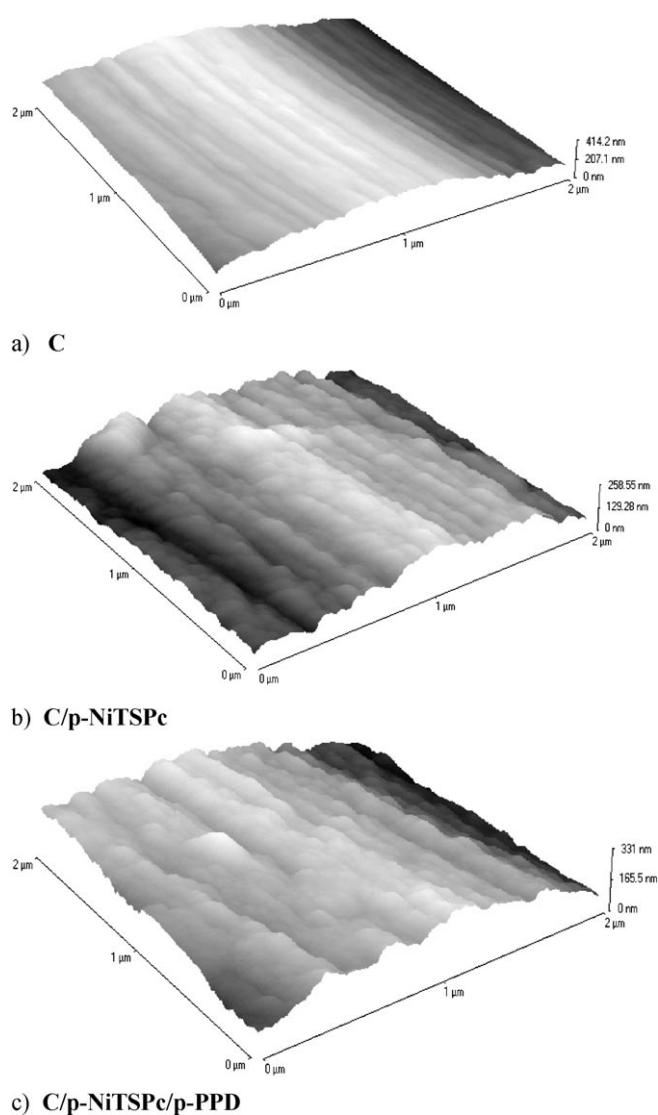


Fig. 6. 3D AFM images of the unmodified (a), modified C/p-NiTSPc (b) and modified C/p-NiTSPc/p-PPD (c) CFME.

deposition of 2×10^{-9} mol/cm² which corresponds approximately to a thickness of 30 nm, as reported elsewhere [50, 52].

We can conclude that the geometrical effect due to an hypothetical increase in geometrical area to roughness modification is not valuable presently because of the decrease of the roughness in presence of p-NiTSPc film. Then the electropolymerized p-NiTSPc film shows a clear electrocatalytic activity towards MPT and PNP redox process, as recently reported for p-NiTSPc film with MPT

Table 2. Average roughness data *Ra* in nm for the three modified homemade CFMEs AFM analysis window : 2×2 μ m, in contact mode under dried samples.

CFME type	C unmodified	C/p-NiTSPc	C/p-NiTSPc/p-PPD
<i>Ra</i> nm \pm 5	81	47	52

Table 3. Sensitivity values and *DL* obtained in 0.1 M acetate buffer pH 5.2; frequency = 60 Hz; scan increment = 10 mV; pulse height = 60 mV.

Type of CFME	Sensitivity (nA L mg ⁻¹) [a] ± 5	Detection limit <i>DL</i> [b] (µg/L) ± 20
C unmodified	20	100
C/p-NiTSPc	80	40
C/p-NiTSPc/p-PPD	32	140

[a] PNP concentration range, 0.01 to 10 mg L⁻¹; [b] ratio signal/noise = 2

[28] and for p-CoTSPc with paraquat and MPT [32, 36]. Furthermore the decrease in the roughness should also be an advantage for the future by limiting the adhesion of (bio)fouling compounds responsible of dramatic decrease of the riverine sensors performances during time, as recently reported [53].

We have also determined the resolution (*R*) of the two peaks from the Figure 5 analysis, with and without p-NiTSPc. In the present case we have defined this parameter as

$$R = 2(E_{p2} - E_{p1}) / (W_1 + W_2) \quad (3)$$

with E_{p2} = the peak potential for PNP, E_{p1} = peak potential for MPT, W_1 and W_2 are the widths at the base of peaks 1 and 2.

Usually in chromatography analysis acceptable resolution is on the order of $R = 1.0$, and baseline resolution between two peaks requires an $R > 1.5$. Presently we obtained $R_{\text{unmodified}} = 1.5$ and $R_{\text{C/p-NiTSPc}} = 1.3$. Then we can consider that the peaks are well separated with an acceptable resolution.

Furthermore the gain in term of sensitivity to the C/p-NiTSPc CFME is nonnegligible in comparison to the unmodified ones. As reported in the Table 3 the sensitivity increases 4 times and the *DL* obtained is 40 µg/L in comparison to 100 µg/L obtained on the unmodified electrode. Similarly catalytic effect was obtained by Goux et al. [51] with Ni-tetraaminophthalocyanine films electrodeposited in dimethylformamide for dopamine electrooxidation. Recently Zagal et al. reported that p-NiTSPc film elaborated and cycling in NaOH is in the form of β-Ni(OH)₂ very similar to that in nickel hydroxide [47].

3.2. Selectivity Increase for the Modified C/p-NiTSPc and C/p-NiTSPc/p-PPD CFMEs

A typical example of the cyclic voltammograms deposition of a p-PPD coating is shown in Figure 7 during 10 cycles of electropolymerization. Figure 7 shows a rapid decrease in the current intensity at 0.3 V/SCE corresponding to an ultrathin film growth of p-PPD. As detailed by Fays et al. [49], the first step of the mechanism of deposition is the adsorption of PPD on the surface electrode. Then this monomer is oxidized with the loss of an electron and the

formation of a cation radical. This step is followed by the cleavage of the C–N bond with formation of a primary carbocation, which is attacks another molecule of PPD. After the expulsion of the proton from the protonated amine, an additional loss of an electron and C–N bond cleavage take place. Therefore poly-PPD, $-(C_6H_4-NH)_n$, grows progressively on the electrode surface. As reported elsewhere for o-PPD coating [46], the measured of the mass variations, obtained during 500 s at a fixed potential of 0.9 V/SCE shows a regular increase of the mass uptake during the first 120 s, followed by a slight stabilization. These two observations may be explained by the fact that the insulating poly-PPD films are generally known to be uniform, very compact and adherent to the electrode surface and growth thick enough until the surface of the electrode is completely covered.

Figure 5 reported also the detection of PNP in presence of MPT when the previously described CFME C/p-NiTSPc is coated by an outer membrane in p-PPD. We observed first that MPT signal disappeared near completely as the PNP peak increase 2 times. This observation illustrates the properties of such neutral electroformed composite film which are forming thin, insoluble, stable, reproducible and adherent films on electrode surfaces [48], possessing a nanoporosity very usable to increase sensors selectivity between low molecular mass molecules [46, 48].

In term of roughness, as reported in Table 2, no modification of *R_a* is observed in presence of p-PPD film due to the fact that a very thin coating of p-PPD was deposited. As observed on the Figure 6, 3D-images 6b and 6c of the C/p-NiTSPc and C/p-NiTSPc/p-PPD modified electrodes surfaces, respectively, have shown no significant change in topography, illustrating properly the low thickness of such electropolymerized neutral films. The peak current decreases to a minimum, because the monomer cannot penetrate the film anymore.

Another observation deals about the degree of hydrophobicity of the outer neutral membrane which is directly correlated to the sensitivity parameter of the microsensor. Previously work have shown that hydrophobic outer membrane has facilitated NO partition across Nafion membrane [48]. Then the main forces dominating the sensitivity of a composite neutral polymer are hydrophobic/hydrophilic interactions, which permits to hydrophobic molecule to pass better across hydrophobic coating and participate to analyte concentration onto the electrode. In our case those forces could not dominate the selectivity, but they work sufficient role due to the positive interaction between the hydrophilic property of the outer membrane (due to their –NH₂ terminal. groups) in presence of the hydrophilic compound PNP (see K_{ow} values of both compounds in the Table 1). Then the observed peak increases for the modified c/p-NiTSPc/p-PPD CFME and should be attributed, to a little part, to the hydrophilic affinity of the outer membrane with PNP. As a perspective, this result will push us to engage further experiments dedicated to preelectrolysis time modulation with the aim to increase the sensitivity of the new p-NiTSPc/p-PPD CFME.

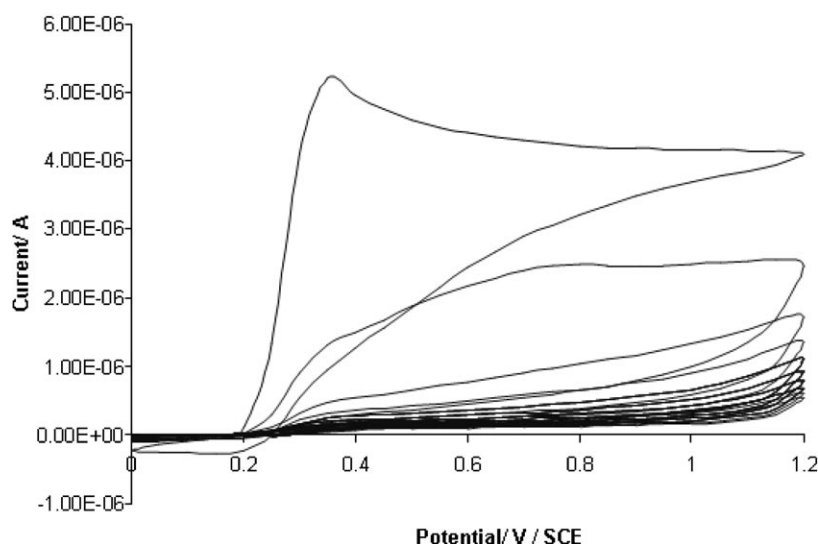


Fig. 7. Cyclic voltammograms for the oxidation of 5 mmol/L *p*-PPD at a carbon microfiber coated in deaerated acetate buffer solution 0.2 mol/L, pH 5.2 at potential scan rate 100 mV/s and 10 repeated cycles.

3.3. Stability Tests Conducted on the New C/p-NiTSPc/p-PPD CFME

Stability tests were engaged on the new C/p-NiTSPc/p-PPD CFME by immersion of this sensor into acetate buffer during 3 weeks. We can observe in Figure 8 that the signal of MPT is very low (large peak centre to 0 V/SCE) as the PNP appeared with a very high and sharpen peak which is centered as observed before to 0.2 V/SCE. After 3 weeks, the noise decreases (baseline appeared smoother), and PNP is always high and sharpen and center to 0.2 V/SCE with a double intensity.

In terms of sensitivity, Figure 8 shows also the evolution of I_p vs. PNP concentration in the range 0.1 to 3 mg/L. The initial equation of the C/p-NiTSPc CFME gives us the following equation for the sensor C/p-NiTSPc (see Table 3):

$$I_p \text{ (nA)} = 77c \text{ (mg/L)} + 0,71 \quad (4)$$

In presence of *p*-PPD coating the sensitivity decrease and we obtained a value of 37 nA L mg^{-1} . After three weeks immersion in acetate buffer, the sensitivity obtained was 35 nA L mg^{-1} . Then the modified electrode exhibited good stability (loss of sensitivity after 3 weeks around 5%) and could be applied as an amperometric sensor for selective determination of PNP in presence of MPT.

4. Conclusions

A novel modified carbon fiber microelectrode (CFME) was obtained by combination of tetrasulfonated nickel phthalocyanine (p-NiTSPc) electroformed film with *para*-phenyl-

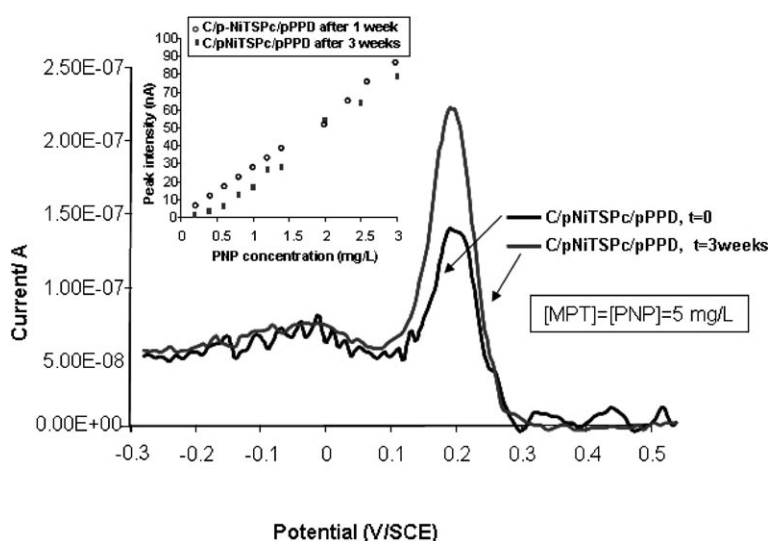


Fig. 8. Stability test vs. time immersion in acetate buffer during 3 weeks.

enediamine (p-PPD) electropolymerized coating. This electrode is dedicated to the organophosphates compounds (OPs) methyl-parathion (MPT) and *para*-nitrophenol (PNP). Our contribution shows that both OPs can be determined simultaneously on the unmodified and modified by p-NiTSPc (denoted C/p-NiTSPc) CFMEs. A clear electrocatalytic activity towards both MPT and PNP redox process was observed for the first time in presence of p-NiTSPc (sensitivity of the C/p-NiTSPc CFME 80 nA L mg⁻¹ in the concentration range 0.01 to 10 mg/L and a detection limit of 40 µg/L). Furthermore the combination of p-NiTSPc and p-PPD electrodeposited films (denoted C/p-NiTSPc/p-PPD) show, for the first time, the possibility to discriminate between MPT and PNP, with MPT under sieving mechanism of exclusion by nanoporosity properties of the outer membrane. Stability experiments were also conducted for 3 weeks in acetate buffer showing a good reproducibility of the sensitivity to PNP vs. time in presence of MPT and a little loss of sensitivity (5%) after 3 weeks.

To increase the sensitivity of the new sensor elaborated C/p-NiTSPc/p-PPD preelectrolysis time treatment should be tested. On the other hand the interest in direct cathodic determination of the OPs should also be compared to the indirect anodic determination for different current sample electrochemical technology SVW in comparison to DPV (differential pulse voltammetry). For rapid analyses under field conditions, direct determination and in situ of OPs it is urgent to elaborate rapid warning and field deployment, more compact low-cost instruments, coupled to smaller sensing probes. Such tool is highly desirable for facilitating the task of on-site monitoring of OP compounds and other pesticides families observable in electrochemistry for portable determinations under low cost.

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