Talanta 81 (2010) 972–979

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Electrochemical analysis of methylparathion pesticide by a gemini surfactant-intercalated clay-modified electrode

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ARTICLE INFO

*Article history:*
Received 26 October 2009
Received in revised form 21 January 2010
Accepted 22 January 2010
Available online 1 February 2010

*Keywords:*
Gemini surfactant
Organoclay
Methylparathion
Clay film-modified electrode
Voltammetry

ABSTRACT

In this study, an hybrid material obtained by the intercalation of a gemini surfactant between the layers of smectite-type clay, was fully characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR) and $N_2$ adsorption–desorption experiments (BET method). To ascertain the intercalation process of the starting clay by the dimeric surfactant, the permselectivity and ion exchange properties of the organoclay were investigated by ion exchange voltammetry using $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$ as redox probes, by the means of a clay film-modified electrode. Due to its organophilic character, the surfactant-intercalated complex was evaluated as electrode modifier for the accumulation of methylparathion (MP) pesticide. The electroanalytical procedure involves two steps: preconcentration under open-circuit followed by voltammetric detection by square wave voltammetry: the peak current obtained (after 5 min preconcentration in $4 \times 10^{-5}$ mol L$^{-1}$ MP) on a glassy carbon electrode coated by a thin film of the modified clay was more than five times higher than that exhibited by the same substrate covered by a film of the pristine clay. This opens the way to the development of a sensitive method for the detection of the pesticide. Many parameters that can affect the stripping response (surfactant loading of the hybrid material, film composition, pH of the detection medium, preconcentration time, electrolysis potential and duration as well as some other instrumental parameters) were systematically investigated to optimize the sensitivity of the organoclay-modified electrode. After optimization, a linear calibration curve for MP was obtained in the concentration range from $4 \times 10^{-7}$ to $8.5 \times 10^{-6}$ mol L$^{-1}$ in acetate buffer (pH 5), with a detection limit of $7 \times 10^{-8}$ mol L$^{-1}$ (signal-to-noise ratio equal to 3). The interference effect of various inorganic ions likely to influence the stripping determination of the pesticide was also examined, and the described method was applied to spring water analysis.

## 1. Introduction

Methylparathion (MP) is an organophosphorous compound widely used as pesticide in agricultural activities [1]. Its high toxicity towards a wide range of organisms has led to its extensively use against pests in a large variety of crops such as bulbs, cereals, fruits, coffee or potato [2,3]. However, pesticides are known as highly toxic chemicals, and the use of MP presents some negative effects for the environment. In fact, during and after their application in a farm, pesticides are transported by wind or water to surrounding compartments as only a part of the applied amounts is bioactive. This transport results in hazardous concentrations of pesticides and their metabolites in the surface water and soils, owing to their low solubility and bioaccumulation properties [4,5]. Several analytical techniques have been used for the analysis of pesticides; they include ultraviolet spectroscopy, capillary electrophoresis, spectrophotometry and mainly gas or liquid chromatography [2,6–8]. These techniques operate quite well but they present a certain number of disadvantages: separation processes in the samples pretreatment are often complex, they often necessitate long analysis times, and most of them require expensive equipment [9,10].

For the past decade, works devoted to the implementation of electrochemical devices suitable for the detection and the sensing of pesticides have gained growing interest, their main purposes being the development of convenient sensitive, selective and rapid electroanalytical techniques [11]. Along these lines, chemically modified electrodes in which the modifier is either a homoionic

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doi:10.1016/j.talanta.2010.01.049

smectite-type clay or an organoclay coated on the surface of a solid substrate have been extensively explored. Some related relevant works were carried out by Manisankar et al. who investigated the electrochemical determination of some pesticides using pure montmorillonite clay-modified glassy carbon electrode, either in the absence or in the presence of a surfactant [12]. These authors also used a conductive polymer modified electrode to study by square wave voltammetry the electrochemical behavior of some common pesticides [13], and more recently, they used a glassy carbon electrode coated with polymer/multiwalled carbon nanotubes for the same purpose [14]. Some other electrochemical pathways were successfully developed for the detection of pesticides: these include stripping voltammetry using either a carbon paste electrodes [9,15,16], or a thin film-modified electrode [10,17]. Despite these interesting results, there is still a need to develop low cost electrochemical sensor that could improve the analytical response of target pollutants and provide valuable information concerning their quantification and their detection, especially in environmental matrices where they are present at trace level. In that context, a possible venue is the resort to electrodes modified with materials prepared by the intercalation of surfactants between swelling clays sheets. Surfactants are actually known to exhibit a great adsorption capacity, and their intercalation in layered clays can make their surface hydrophobic, that is let them turn organophilic [5]. Such organoclays are likely to sorb neutral hydrophobic molecules via a non-polar interaction between the organic phase of the surfactant–clay complex and the hydrophobic organic moieties [18–20]. The sorption mechanism of organics by organoclays is documented, and it is established that the affinity of these sorbents towards the sorbates depends upon the properties of the organic molecule (solubility, polar character, and partition coefficient) and the molecular structure of the surfactant (length of the alkyl chain, critical micelle concentration, ionic nature, density, and aggregation degree) [21–23]. Yet, several works have been reported on the modification of swelling clays by various alkylammonium cations, followed by the applications of the obtained organoclays to the sorption of neutral organic compounds [24–27]. However, to the best of our knowledge, the exploitation of clay modified by the intercalation of a dimeric surfactant (i.e. gemini surfactant bearing two hydrophobic and two hydrophilic groups in the same molecule) in connection to the electroanalysis has not yet been reported. In this work, we have thus investigated the use of a gemini surfactant-intercalated smectite-clay as modifier of a glassy carbon electrode for the electroanalysis and detection of the MP pesticide by square wave voltammetry.

## 2. Experimental

### 2.1. Clay mineral and its pretreatment, chemicals and reagents

The clay mineral used in this study (namely "Ba") was a smectite collected from Baba hills (West-Cameroon, Central Africa). Its chemical composition and structural formula are provided elsewhere [28,29]. It is characterized by a cation exchange capacity (CEC) of 89 mequiv. per 100 g and a specific surface area ($N_2$ adsorption–desorption, BET) of 155 $m^2\,g^{-1}$. The study was carried out on the $\leq 2\,\mu m$ clay fraction obtained by wet sedimentation. Before its modification, the clay was converted into the sodium homoionic form according to procedures previously described [29,30]. Briefly, 5 g of the clay crushed and sieved at 80 μm were dispersed in 200 mL of 1 mol $L^{-1}$ NaCl solution, and stirred mechanically for 8 h. The clay suspension was centrifuged at 5000 rpm for 10 min, and the supernatant discarded. To ensure the complete conversion of the clay to its homoionic form, the solid phase was contacted again to 200 mL of fresh NaCl molar solution and the resulted suspension maintained under constant stirring overnight. Afterwards, the solid was filtered and washed several times with distilled water until a negative test for $Cl^-$ ions was achieved (using 0.1 mol $L^{-1}$ $AgNO_3$). Upon this stage, the clay particles were dispersed in 200 mL of water and the suspension was placed in a sedimentation tube, the fraction below 2 μm was then separated by sedimentation according to Stockes law, recovered and dried on paper filter at room temperature for 24 h. This sodic form of the clay will hereafter be referred as $Ba\text{-}Na^+$.

The gemini surfactant P-phenylenedimethylene bis dodecyl-N,N dimethylammonium dibromide ($C_{10}H_{21}N(CH_3)_2–CH_2–C_6H_4–CH_2–N(CH_3)_2C_{10}H_{21}Br_2$, denoted hereafter as $D0^{2+}$) was synthesized according to the procedure previously described by Rosen and Song [31]. Its purification was performed by repeated recrystallization from chloroform–acetone mixtures. Its structure was ascertained by $^1H$ NMR spectrum (result not shown) and Fourier transform infrared spectroscopy.

All chemicals and reagents used in the electrochemical section were of analytical grade, and used as received. Methylparathion was purchased from Supleco (France), and a stock solution ($10^{-2}$ mol $L^{-1}$) was prepared in ethanol. $K_3Fe(CN)_6$ (>99%, Prolabo) and $Ru(NH_3)_6Cl_3$ (Alfa) were reagent grade and used as received. An acetate buffer solution was used as supporting electrolyte and was prepared by mixing 0.1 mol $L^{-1}$ $CH_3COONa$ and $CH_3COOH$ (Riedel-de-Haën). The pH was adjusted by NaOH and HCl (37%) purchased, respectively, from BDH and Prolabo. All the aqueous solutions were prepared using double distilled water.

### 2.2. Preparation of the surfactant–clay composites and their characterization

The synthesis of the surfactant–clay composites was undertaken according to the following procedure: 4 g of the homoionic $Ba\text{-}Na^+$ material were dispersed in 400 mL of deionized water to which a desired amount of P-phenylenedimethylene bis dodecyl-N,N dimethylammonium dibromide alcohol solution was added. The concentrations of the gemini surfactant were 0.25 CEC, 0.50 CEC, 0.75 CEC or 1 CEC of the starting clay. The reaction mixtures were stirred for 48 h at 60 °C, cooled and washed from bromide with water until a negative test (using 0.1 mol $L^{-1}$ $AgNO_3$) was observed. The organoclays prepared at the concentration 0.25 CEC, 0.50 CEC, 0.75 CEC and 1 CEC are, respectively, identified as $Ba\text{-}DO_1$, $Ba\text{-}DO_2$, $Ba\text{-}DO_3$ and $Ba\text{-}DO_4$ throughout the text. The homoionic clay and its dimeric–surfactant derivatives were subsequently characterized by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and specific surface area measurements (by Brunauer–Emmett–Teller (BET) method).

XRD patterns were recorded at room temperature using a classical powder diffractometer (X'PERT PRO/Philips) equipped with a Cu anode (quartz monochromator, $k\alpha_1$ radiation, $\lambda = 1.54056$ Å). Diffuse reflectance infrared spectra were recorded between 4000 and 1250 $cm^{-1}$, using a FTIR PerkinElmer 2000 spectrometer equipped with a DTGS detector. The samples were analyzed at room temperature using KBr pellets (clay or organoclay mass fraction <10%). The diffuse reflectances $R_s$ of the sample and $R_r$ of KBr used as non-absorbing reference powder were measured in the same conditions. The spectrum resolution was 4 $cm^{-1}$ and the accumulation time was 5 min. The spectra recorded are displayed in a pseudo-absorbance scale (i.e. $\log R$, where $R = R_s R_r^{-1}$ is the clay reflectance). BET analysis was performed by measurements of $N_2$ adsorption–desorption isotherms, at 77 K on a Coulter Instrument (model SA 3100). Prior to the analysis, the samples were degassed overnight. The surface areas were calculated using the BET equation [32].

### 2.3. *Working electrode preparation, electrochemical equipment and procedures*

The clay-modified working electrode was prepared as follows: the glassy carbon electrode (GCE) was first polished with an aqueous suspension of 0.05 μm alumina and ultrasonically cleaned for 5 min in a 1/1 ethanol:$H_2O$ mixture, then rinsed with distilled water and dried at room temperature. Aliquots of 20 μL of a suspension containing appropriate amounts of the (organo)clay were deposited by drop coating on the active surface (3 mm in diameter) of the GCE. The clay-modified electrode was stored at room temperature for about 6 h to ensure their complete drying before use. Cyclic voltammetry and square wave voltammetry measurements were conducted with a μ-autolab potentiostat equipped with the GPES electrochemical analysis system (Eco Chemie, Holland), and connected to a computer. A classical three-electrode system comprising a tungsten wire as auxiliary electrode, a SCE reference electrode and the (organo)clay film working electrode was used. The pH measurement was performed with analog pH meter/model 301. Dearation was performed by purging with nitrogen for 15 min. Multisweep cyclic voltammograms were recorded at room temperature, by immersing the working electrode in the "analyte + electrolyte" solution, at a scan rate of 100 mV s$^{-1}$ unless otherwise stated. The electrochemical procedure for MP analysis by stripping voltammetry involved two successive steps: an open-circuit accumulation followed by a voltammetric detection in a separate medium. Preconcentration was achieved by dipping the working electrode in a beaker containing an aqueous solution of MP at a given concentration. The solution was kept under constant stirring, and after a predetermined time, the electrode was promptly removed, rapidly rinsed with water and transferred into the electrochemical cell containing the detection solution where the accumulated species of MP were analyzed by square wave stripping voltammetry. Prior to the next measurement, the electrode was regenerated by transferring in a blank acetate buffer solution (pH 4.8) left under mild stirring, where trace amounts of MP were observed to totally desorb after 60 s.

In order to achieve the best conditions for MP detection at the organoclay-modified electrode, SWV parameters were studied and optimized. These parameters include the frequency, the step potential, the electrolysis potential and duration. They are interrelated and have a combined effect on the stripping response. Thus, each of them was properly scrutinized, and the most suitable values (i.e. those leading to a maximum SWV signal) chosen for the determination of MP are as follows: frequency: 50 Hz, step potential: 5 mV, electrolysis potential: −0.8 V, electrolysis duration: 15 s.

## 3. Results and discussions

### 3.1. *Characterization of the organoclays*

Fig. 1 presents the XRD patterns of Ba-Na$^+$, before and after its modification by the gemini surfactant at loading capacities between 0.25 and 1 CEC. Besides the intrinsic signals due to the framework of clay platelets (i.e. $2\theta = 12.28$, $2\theta = 19.82$), the diffractogramm of the pristine clay reveals a broad peak (0 0 1), indicating a poorly crystallized material with a *d*-spacing (distance between clay sheets) of 10.1 Å. Upon intercalation, the basal spacing is expanded as expected, depending on the dimeric surfactant initial concentration. Yet, surfactant derivatives of smectites have been investigated by numerous authors, and it is well known that long surfactant chains can adopt a monolayer, a bilayer or a pseudotrimolecular arrangement between the clay layers depending on the density of the clay charge and the proportion of the CEC occupied [33–35]. In Fig. 1, at loading level of DO$^{2+}$ equal to 0.25 CEC (Ba-DO$_1$), the $d_{001}$ value is 12.1 Å, the corresponding peak is significantly broader suggesting a coexistence of reflections corresponding to the interlayer distances of 10 and 12 Å, i.e. a randomly distribution between the clay sheets and the surfactant molecules. The organoclays with surfactant concentration equal to 0.5 and 1 CEC present symmetrical peaks, with $d_{001}$ values of 16.2 and 16.6 Å, respectively.

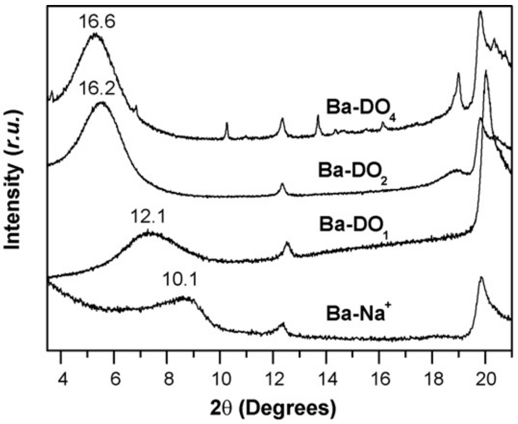


**Fig. 1.** X-ray diffraction patterns of Ba-Na$^+$, Ba-DO$_1$, Ba-DO$_2$, and Ba-DO$_4$ materials.

These observations suggest a monolayer arrangement of the cationic species between the clay platelets, in agreement with the theoretical value of $d_{001}$ for a monolayer configuration of DO$^{2+}$ ions ($d_{001} = 10.1 + 6.5 = 16.6$ Å). The results obtained by XRD therefore confirm the presence of the dimeric surfactant into the clay gallery, in agreement with previous works [24,36,37].

The FTIR spectra of the starting clay and the organoclays (in the 4000–1250 cm$^{-1}$ region) are compared in Fig. 2. In order to identify the contribution of the functional groups on the hybrids materials, the spectrum of the organic modifier alone was also recorded (Fig. 2a). The latter is characterized by the presence of a doublet at 2914 and 2851 cm$^{-1}$, which is assigned respectively to the asymmetric and symmetric stretching of aliphatic $CH_2$ groups. The deformation modes of these groups are also observed between 1500 and 1400 cm$^{-1}$. The infrared spectrum of the blank clay (Fig. 2b) is made of three main bands; those at 3697 and 3626 cm$^{-1}$ are assigned to the stretching vibrational mode of structural hydroxyl groups, while the signal at 1627 cm$^{-1}$ is due to the OH deformation of the interlayer water molecules [38,39,40].

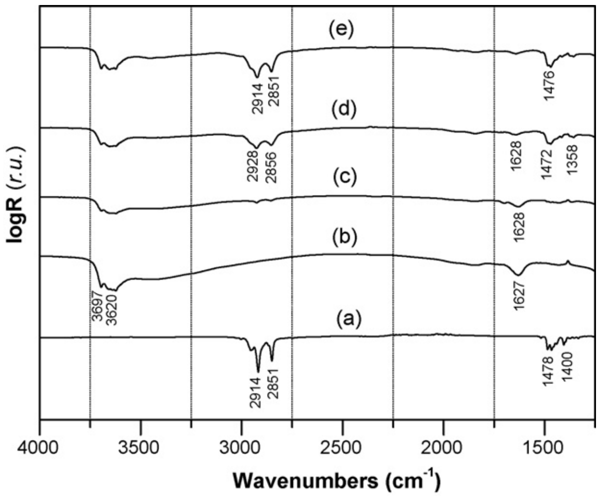


**Fig. 2.** Infrared spectra (4000–1250 cm$^{-1}$ region) of (a) DO$^{2+}$, (b) Ba-Na$^+$, (c) Ba-DO$_1$, (d) Ba-DO$_2$, and (e) Ba-DO$_4$ materials.

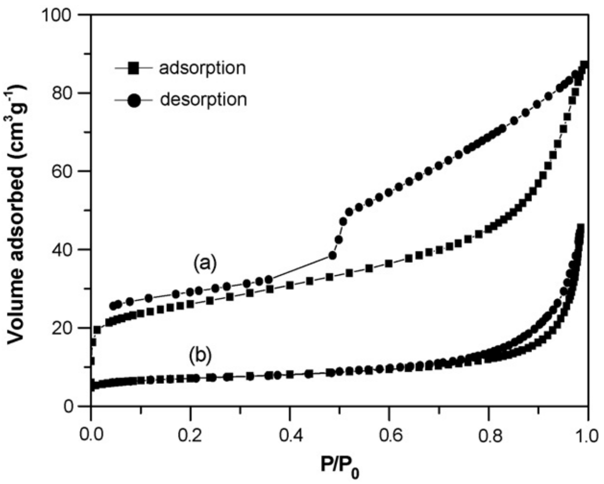


**Fig. 3.** Nitrogen adsorption–desorption isotherms obtained at 77 K for (a) Ba-Na$^+$ and (b) Ba-DO$_4$ materials.

The spectral profile in the 3000–2750 cm$^{-1}$ region of the organoclays changes significantly with the concentration of the gemini surfactant. When the amount of DO$^{2+}$ within the clay platelets is increased, the bands related to the organic modifier observed at 2928 and 2856 cm$^{-1}$ become more pronounced (see Fig. 2c–e). Meanwhile, a decrease in the intensity of the band at 1627 cm$^{-1}$ is noticed, indicating the dehydration of the clay with the intercalation of the organic cations. This confirms the change in the properties of the clay, from hydrophilic (pristine clay) to organophilic (organoclays), upon intercalation.

Nitrogen adsorption–desorption isotherms of the crude clay and the Ba-DO$_4$ organoclay are depicted in Fig. 3. On the isotherm of Ba-Na$^+$ clay material (Fig. 3a), the desorption branch follows a different path to the adsorption curve, leading to a large hysteresis loop which is illustrative of a mesoporous structure with a contribution from micropores [32,41]. This isotherm is intermediate between types II and IV, with H$_3$ hysteresis loop according to IUPAC classification [40,41,42].

Upon modification by intercalation of the gemini surfactant cations, the shape of the isotherms changes significantly as illustrated by the curve in Fig. 3b for Ba-DO$_4$, the main feature being the decrease in the specific surface area, from 155 m$^2$ g$^{-1}$ (pristine clay) to 6 m$^2$ g$^{-1}$ (intercalated material). These observations supported the idea that nitrogen is not easily accessible to the interlayer space of the organoclays, which is occupied by the intercalated organic species.

### *3.2. Electrochemical characterization of the organoclay by permeation studies*

In order to collect more information about the porosity and the influence of the functional groups of the organoclays, their ion exchange and permselectivity properties were studied by means of clay film-modified electrodes. It is well known actually that the use of an ion-exchanger as electrode modifier constitutes a strategy to enhance the local concentration of ionic redox probes at (organo)clay-modified electrodes [43,44]. The raw clay in one hand and its organically modified form in the other hand were thus coated onto GCE surfaces, and the resulting electrodes were applied to the uptake/rejection of [Fe(CN)$_6$]$^{3-}$ and [Ru(NH$_3$)$_6$]$^{3+}$ ions used as redox probes. Prior to this experiment the probes were first analyzed at a bare GCE, and gave rise to the expected defined reversible cyclic voltammograms of constant intensity upon continuous cycling (results not shown). The results obtained with the clay-modified electrodes are illustrated in Fig. 4. On the GCE coated

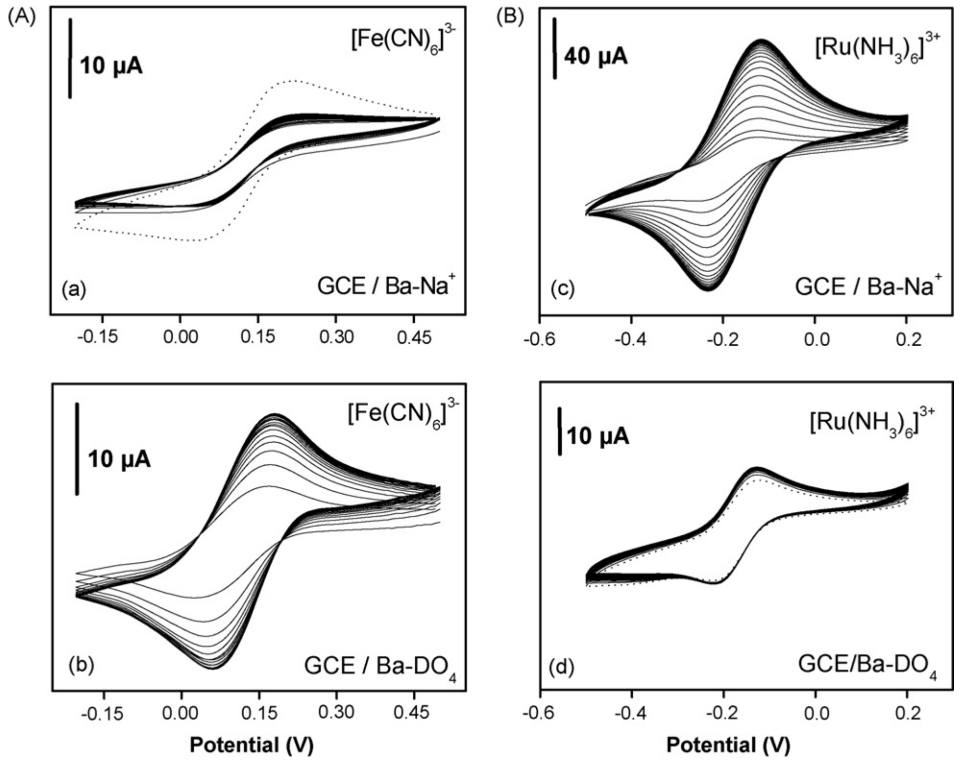


**Fig. 4.** Multisweep cyclic voltammograms recorded at 50 mV s$^{-1}$ (A) in 0.1 mol L$^{-1}$ NaCl + 1.5 × 10$^{-3}$ mol L$^{-1}$ [Fe(CN)$_6$]$^{3-}$ using a GCE coated with (a) Ba-Na$^+$, and (b) Ba-DO$_4$ materials and (B) in 0.1 mol L$^{-1}$ NaCl + 1.5 × 10$^{-3}$ mol L$^{-1}$ of [Ru(NH$_3$)$_6$]$^{3+}$ on the GCE coated with a thin film of (c) Ba-Na$^+$, and (d) Ba-DO$_4$. The dotted line on (a) and (d) represent the signal of [Fe(CN)$_6$]$^{3-}$ and [Ru(NH$_3$)$_6$]$^{3+}$, respectively, on the bare GCE).

with a film of Ba-Na$^+$ clay (Fig. 4a), $[Fe(CN)_6]^{3-}$ gives rise to stable CVs whose mean intensity (3.4 μA) is lower than that obtained at the bare GCE (7.5 μA), i.e. a decrease of about 45% from the bare electrode to the modified one. Such behavior is due to electrostatic repulsions between the negatively charged clay platelets and the analyte [45].

When the GCE is modified with Ba-DO$_4$, continuous potential cycling in the same conditions leads to an increase in peak current (Fig. 4b). The peak current reaches its maximum steady-state value after 15 cycles, and the current was 3.6 times higher than that recorded on the pristine sodium clay film, indicating thereby an effective preconcentration capability for anionic species of the Ba-D0$_4$ material. This behavior can be due to the aggregation upon the modification of the organic cations, via both ion exchange and hydrophobic bonding, leading to the appearance of positive charges in the clay layers and on the clay surface, thereby inducing uptake of anionic species [46,47]. When the same experiment was performed with the charged redox probe $[Ru(NH_3)_6]^{3+}$, repetitive scans resulted in a slight faradic response that did not increase in peak height (Fig. 4d); the steady-state currents recorded correspond almost to those displayed by the bare GCE. As suggested by others [46,48], the probe enters the film mainly through small pinholes and DO$^{2+}$ competes with the surfactant cation for the ion exchange sites. However, if the GCE is covered by a film of pristine clay Ba-Na$^+$ instead of Ba-DO$_4$, the CV peaks increase ca. 4-fold relative to that obtained at the bare GCE (Fig. 4c), due to more favorable ion exchange. So, the analysis of the results in Fig. 4 support the idea that the uptake of $[Fe(CN)_6]^{3-}$ or $[Ru(NH_3)_6]^{3+}$ is controlled by an ion exchange process, mainly governed by the charge of the GCE modifier, and somewhat by the porosity of the film coated onto the electrode.

### 3.3. Electrochemical behavior of MP on the organoclay-modified electrode

In order to study the electrochemical behavior of MP on the GCE modified with the organoclay, repetitive cyclic voltammetry was conducted in 0.1 mol L$^{-1}$ acetate buffer (pH 5). Fig. 5 presents the voltammogramms of $41.5 \times 10^{-6}$ mol L$^{-1}$ MP, on the GCE coated with either the raw clay or its organically modified form. In both cases, the electrochemical response is made of two redox systems: a pair of reversible peaks ($E_{a1} = 0.03$ V and $E_{c1} = 0.00$ V), and an irreversible reduction peak ($E_{c2} = -0.60$ V). It should be noted that during the first cathodic scan (dotted line in Fig. 5), the peak of the reversible system did not appear, but arises only when the second cathodic peak was formed: the reversible system thus resulted from a species generated by the irreversible system. Such a behavior was previously reported for MP on a carbon paste electrode [15] and on a nafion coated GCE [17], and the irreversible peak was attributed to the reduction of the nitro-group of MP to hydroxylamine group (Eq. (1)), whereas the reversible system correspond to an electron transfer process mentioned by Eq. (2) [10,15,17]. Apart from this common trend, the other cyclic voltammetry characteristics of MP exhibited by the GCE modified by Ba-Na$^+$ and Ba-DO$_4$ were quite different.

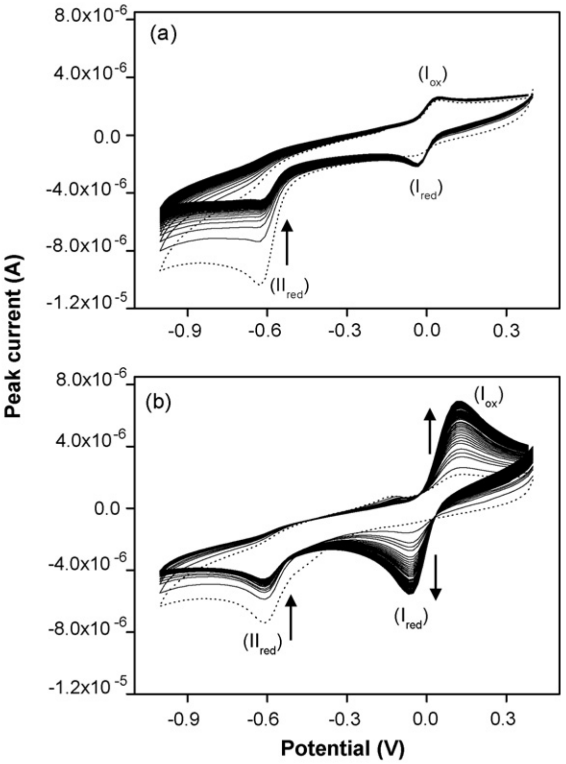
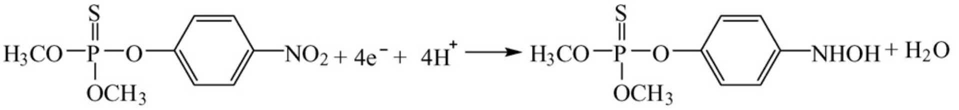


**Fig. 5.** Multisweep cyclic voltammograms recorded in 41.5 μM MP in 0.1 mol L$^{-1}$ acetate buffer (pH 5) on the GCE coated by (a) the Ba-Na$^+$ clay and (b) by the Ba-DO$_4$ organoclay film. Potential scan rate: 100 mV s$^{-1}$.

As a matter of fact, the accumulation of MP on the raw clay-modified electrode (Fig. 5a) was quite difficult as evidenced by the rather constant intensity of the peaks of the reversible peak system. This is not surprising since MP is an organic molecule slightly soluble in water, with little affinity towards hydrophilic matrix. On the opposite, the organoclay-modified electrode showed high capability to accumulate MP.

As can be seen in Fig. 5b, continuous cycling potentials induces a dramatic increase in peak currents of the reversible system that reached a steady-state value after about 30 cycles. The presence on the GCE of the organophilic modified clay film favored the accumulation of MP. To yield more insights in the electrochemical behavior of MP further experiments were performed including the study of the effect of increasing the potential scan rate. The voltammograms obtained under the same conditions as in Fig. 5 are depicted in Fig. 6 from which it appears that the peak current increases with the potential scan rate ($\nu$). A plot of the anodic peak current ($I_{pa}$) of the reversible system versus $\nu^{1/2}$ exhibits a linear dependence (graph not shown). The charge transfer process at the organoclay-modified electrode is thus a diffusion-controlled one. From the above results, it appears that Ba-organoclays used as electrode modifiers can be suitable for building an electrochemical sensor for MP. This is discussed hereafter.



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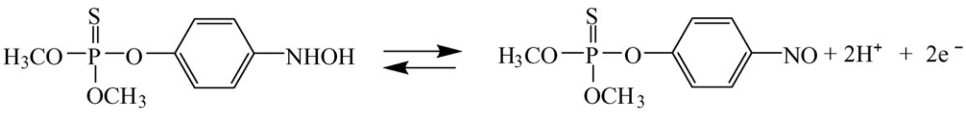

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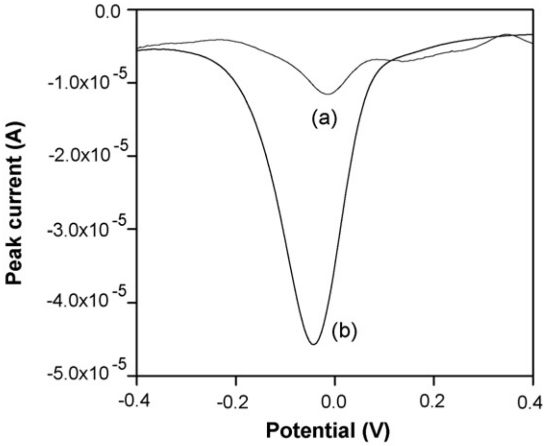

**Fig. 6.** SWV response of $4 \times 10^{-5}$ mol L$^{-1}$ MP in acetate buffer at pH 5, at a GCE coated with a thin film of (a) Ba-Na$^+$ and (b) Ba-DO$_4$. Other experimental conditions: electrolysis potential: −0.8 V, electrolysis duration: 12 s, frequency: 50 Hz, pulse amplitude: 50 mV.

Fig. 6 presents the SWV curves of a $4 \times 10^{-5}$ mol L$^{-1}$ MP solution at a GCE coated with the unmodified clay or the surfactant-intercalated clay. A well-defined but rather low peak was obtained in the potential range −0.4 to 0.4 V with the sodium montmorillonite clay (Fig. 6a), pointing out the weak sorption capacity of the raw clay towards MP. When the GCE was modified by coating with a film of Ba-DO$_4$, its sensitivity was significantly improved (Fig. 6b), due to the high affinity between the organophilic material and MP as already stated (vide supra). The peak current measured from the extrapolated base line for the later was found to be equal to 42 μA, that is more than five times higher than at the pristine clay film electrode where the recorded value was about 7.5 μA.

The operational stability and reproducibility of the coatings at the GCE were also evaluated, and highly reproducible signals were obtained from repetitive experiments upon MP detection in acetate buffer (pH 5). Thus, for a series of five successive measurements of the same $3 \times 10^{-5}$ mol L$^{-1}$ MP solution, a coefficient of variation of 2% was noticed, indicating good reproducibility of the method. As we observed, one organoclay-modified electrode (OCME) can be used for more than 10 SWV measurements, i.e. for a total of 90 min of analysis time. All the above results illustrated the interest of intercalating the smectite-type clay with the dimeric surfactant, prior to its use as clay film electrode to accumulate MP. The key parameters involved in the stripping process will be now scrutinized in order to optimize the sensitivity of the organoclay-modified electrode with respect to possible use as MP sensor.

## 3.4. Optimization of parameters for MP detection

### 3.4.1. Influence of the gemini surfactant on the stripping process

As far as the evaluation of the performance of an organoclay film electrode is concerned, the study of the effect of the surfactant loading of the hybrid material on the SWV curves appears as a key step. Fig. 7A displays typical response for a $4 \times 10^{-5}$ mol L$^{-1}$ MP solution using the GCE coated by the organoclays with surfactant loadings ranging from 0.25 to 1 CEC (b–e), as well as the raw clay-modified GCE (a). As one can observe, the peak current is substantially enhanced with an increase in the intercalation level of the hybrid material, the maximum response being obtained for 1 CEC (Fig. 7B).

Indeed, increasing the modifying agent in respect to the CEC of Ba enhances the hydrophobic character of the hybrid material; as a consequence resulted the affinity of this material towards species of low solubility in aqueous medium is exalted through hydrophobic-type interactions [49,50]. A DO$^{2+}$ loading of 1 CEC was thus selected as optimal, and the corresponding Ba-DO$_4$ material used for subsequent studies.

The film composition is also expected to affect the electrode response. The effect of the proportion of Ba-DO$_4$ in the aqueous suspension used to modify the GCE is presented in Fig. 7C from which it appears that the highest SWV signal is obtained when an aqueous solution containing about 2 g/L of Ba-DO$_4$ is used. Beyond this optimum value, increasing the proportion of the organoclay lowers the current response, as a consequence of the increase of the film thickness that renders the mass transfer more difficult [16,51].

### 3.4.2. Influence of the pH of the detection medium

The acidity of the detection medium is a key parameter that can affect the mass transport to the electrode surface, especially when the redox process involves some protons as in the present case. In Fig. 8 is represented the evolution of the SWV curve when the detection medium pH is varied. The pH range studied covers only the acidic zone to avoid the hydrolysis of MP which may occur in basic media [2,52].

As one can notice (Fig. 8a), the electrode response was low for the most acidic media (pH 1–3), most probably because the important quantity of protons may somewhat prevent the access of MP to the adsorption sites of the organoclay. A possible degradation of the clay due to the acidic hydrolysis of Al centers (in tetrahedral sheets) can also explain these low current values. At pH values above 3, the electrode signal was found to grow up markedly to reach the highest value at pH 5, and then decreased strongly at pH 6 down to about 20% (in comparison with the highest signal at pH 5). The lower stripping signals recorded for pH 6 can be due to a change of

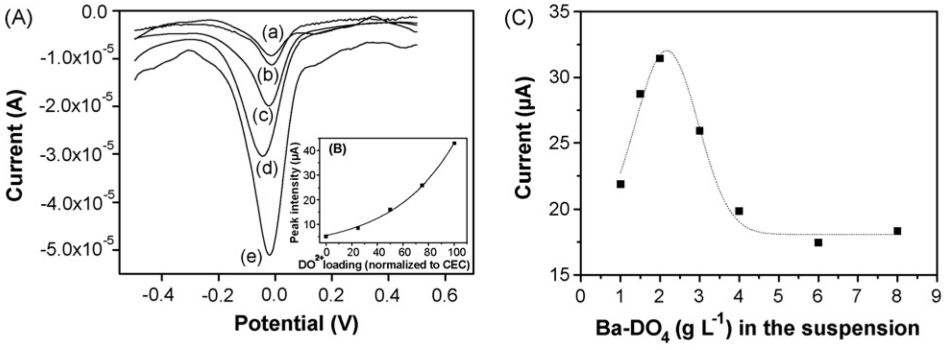

**Fig. 7.** (A) SW voltammetric response for $4 \times 10^{-5}$ mol L$^{-1}$ MP (in acetate buffer, pH 5) obtained on a GCE modified by a coating of (a) Ba-Na$^+$, and the organoclay containing DO$^{2+}$ at (b) 0.25, (c) 0.50, (d) 0.75 and (e) 1 CEC of the starting clay. (B) Variation of peak current with DO$^{2+}$ loading normalized to CEC. (C) Effect of the amount of Ba-DO$_4$ in the suspension used in preparing the organoclay-modified electrode on the peak current of MP. Other conditions as in Fig. 6.

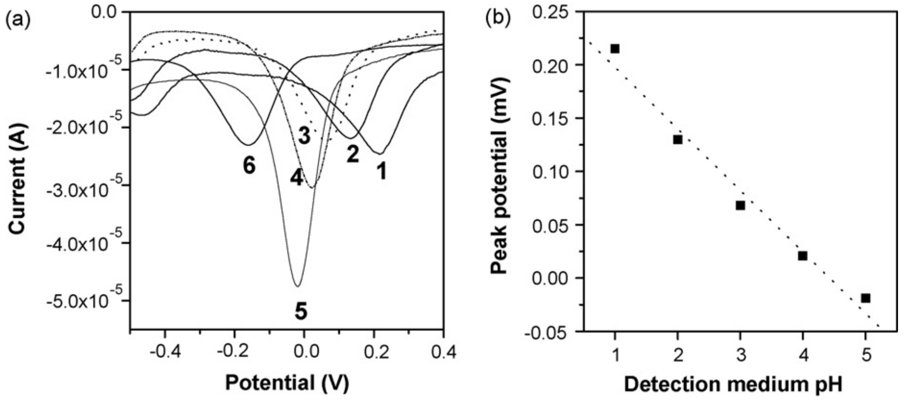

**Fig. 8.** (a) Effect of detection medium pH on the anodic peak current of MP, on a GCE coated by Ba-DO$_4$ (other experimental conditions as in Fig. 6). (b) Variation of the peak potential versus pH of the detection medium.

the electrochemical mechanism (4e$^-$ to 1e$^-$ and 3e$^-$ with the stabilization of NO$_2^{\bullet -}$). The peak potential and the pH show a linear relationship with the regression equation $E_P = -0.058$ pH + 0.225 (Fig. 8b), which implies that the number of electrons and protons involved in the reaction are equal. A solution with pH around 5 was selected as the optimal situation for the detection of the pesticide and used for further experiments.

### 3.4.3. *Influence of the pesticide concentration*

We intended to apply the optimized conditions established throughout the present study along with those mentioned in Section 2, to the quantitative analysis of MP. Fig. 9 depicts typical SWV peaks recorded after 5 min preconcentration (at open-circuit) for a solution containing the pesticide at concentrations ranging from $4.0 \times 10^{-7}$ to $8.5 \times 10^{-6}$ mol L$^{-1}$.

Peak currents increase with MP concentration and, as shown in the inset in Fig. 9; the relationship between these two parameters is linear, with a slope of 0.576 and a correlation coefficient of 0.998. A detection limit of $7 \times 10^{-8}$ mol L$^{-1}$ was evaluated for a signal-to-noise ratio equal to 3. This value is better in comparison to many others gathered from the literature for the electrochemical determination of the same analyte at chemically modified electrodes [2,12], or even for some other pesticides [53–55].

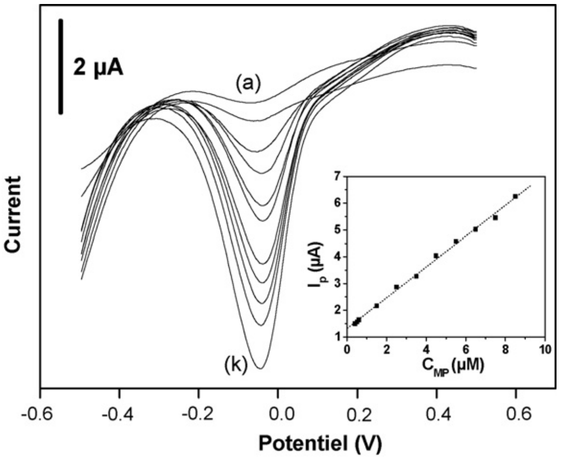

**Fig. 9.** Variation of peak current with MP concentration on glassy carbon electrodes modified with Ba-DO$_4$, from (a) to (k): 0.4, 0.5, 0.6, 1.5, 2.5, 3.5, 4.5, 5.5, 6.5, 7.5 and $8.5 \times 10^{-6}$ mol L$^{-1}$, respectively. The inset shows the corresponding calibration curve.

### 3.5. *Interference study and analytical application to spring water*

The selectivity of the sensor was tested in the presence of various inorganic ions that are likely to influence the stripping signal of MP, especially in water and soils. To this end, known amounts of these ions (with concentration at least 25 times in excess over MP) were added to a solution containing $2 \times 10^{-5}$ mol L$^{-1}$ MP. The resulting solutions were then analyzed and the results obtained after 5 min accumulation are summarized in Table 1.

One can see that, up to 1000-fold excess of K$^+$, NO$_3^-$ and Cl$^-$, no real influence of the MP response was noticed. However, Mg$^{2+}$ and SO$_4^{2-}$ were found to interfere slightly at 500-fold excess while Pb$^{2+}$ and Zn$^{2+}$ at concentration 500 times larger than MP significantly interfered by decreasing the MP signal intensity. The most dramatic situation was observed with Cu$^{2+}$, and mainly with Hg$^{2+}$ species for which the reduction occurred around 0.0 V, i.e. at the same potential as the reduced form of MP. As shown in Table 1, Hg$^{2+}$ was found to interfere seriously by reducing the signal of MP, when added in the preconcentration medium with a concentra-

**Table 1**
Effect of interference ions on the response of the GCE/Ba-DO$_4$ to $2 \times 10^{-5}$ mol L$^{-1}$ MP in acetate buffer (pH 5).

| Interference ions | Added amount over MP concentration | % Variation in the anodic peak current ($I_{pa}$ (MP) = 100%) |
|---|---|---|
| Cl$^-$ | 500 | 0 |
| | 1000 | 0 |
| SO$_4^{2-}$ | 100 | −3 |
| | 500 | −8 |
| NO$_3^-$ | 500 | −2 |
| K$^+$ | 500 | 0 |
| | 1000 | 0 |
| Mg$^{2+}$ | 100 | −3 |
| | 500 | −8 |
| Zn$^{2+}$ | 100 | −7.2 |
| | 500 | −19.6 |
| Pb$^{2+}$ | 100 | −2 |
| | 500 | −16.6 |
| Cu$^{2+}$ | 100 | −2.9 |
| | 200 | −35.3 |
| | 500 | −42.7 |
| Hg$^{2+}$ | 25 | −20.9 |
| | 50 | −57.2 |
| | 100 | −89.1 |

tion 25 times excess over MP. This fact could somewhat reduce the selectivity of the method, and led us to propose the elimination of $Cu^{2+}$ and $Hg^{2+}$ ions from any matrices before the quantification of MP. These findings tend to show that in proper conditions, the sensor can be used for the electroanalysis of MP. To validate the method, the analysis of MP in a real water sample collected downtown Yaounde and stored at room temperature in glass bottles has been carried out. A volume of 50 mL of the spring water sample was first analyzed by using the optimized parameters established so far in this study and MP was not detected. However if the spring water was spiked with $5 \times 10^{-6}$ mol L$^{-1}$ of MP, a recovery amount of $4.83 \times 10^{-6}$ mol L$^{-1}$ was obtained (i.e. 96.6% of the added pesticide). Apparently, the interference effect in this real sample, if any, is almost negligible. Thus, the obtained results clearly indicate that the proposed voltammetric procedure could be applied for MP sensing in environmental polluted media.

## 4. Conclusion

This work was devoted to the preparation of an organoclay material, which was achieved by the insertion of a dimeric surfactant into swelling clay, followed by its characterization by various techniques. Upon its deposition by drop coating onto the surface of a glassy carbon electrode, this hybrid material was successfully applied to the detection of methylparathion. It was found that the sensitivity of this organoclay-modified electrode depends on the film composition and mainly on the parameters involved in the detection step by square wave voltammetry. In spite of rather long time required for organoclay sample preparation, the analytical method developed here remains simple and cheap and is promising for the monitoring of organophosphorous pesticides in various polluted media.

## Acknowledgements

These results were obtained through the support of AIRES-Sud, a programme from the French Ministry of Foreign and European Affairs implemented by the Institut de Recherche pour le Développement (IRD-DSF). The authors also acknowledge the support of the Academy of Science for the Developing World (Grant No. 07-052-LDC/CHE/AF/AC allowed to E. Ngameni's TWAS Research Unit).

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