Talanta 103 (2013) 337–343

Contents lists available at SciVerse ScienceDirect

Talanta

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

Electrochemical determination of mesotrione at organoclay modified glassy carbon electrodes

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ARTICLE INFO

Article history:
Received 19 June 2012
Received in revised form
19 October 2012
Accepted 22 October 2012
Available online 30 October 2012

Keywords:
Clay
Mesotrione
Pesticide
Sensor
Electrode

ABSTRACT

A natural Cameroonian smectite-type clay (SaNa) was exchanged with cationic surfactants, namely cetyltrimethylammonium (CTA) and didodecyldimethyl ammonium (DDA) modifying its physico-chemical properties. The resulting organoclays that have higher adsorption capacity for mesotrione than the pristine SaNa clay, have been used as modifiers of glassy carbon electrode for the electrochemical detection of this herbicide by square wave voltammetry. The stripping performances of SaNa, SaCTA and SaDDA modified electrodes were therefore evaluated and the experimental parameters were optimized. SaDDA gives the best results in deoxygenated acetate buffer solution (pH 6.0) after 2 min accumulation under open circuit conditions. Under optimal conditions, the reduction current is proportional to mesotrione concentration in the range from 0.25 to 2.5 μM with a detection limit of 0.26 μM. The fabricated electrode was also applied for the commercial formulation CALLISTO, used in European maize market.

1. Introduction

Because the population growth will increase, the needs for foods and consequently agricultural activities will become more and more acute. The use of chemicals for higher yields of agricultural crops will be still effective in the near future even though new farming practices more effective emerge. Then the dissemination of pesticides in the environment will still remain a major concern. Indeed, the risks arising on quality of surface and ground waters and soils, on biodiversity and on human health must be better identified and prevented. Traceability of chemical inputs in the various compartments of the environment is an ethic duty that found the environmental national and international regulations. In order to better control the quality of the ground waters and soils and to improve the understanding of the fate of pesticide in environment, accurate and cost effective analytical methods are important. For the past decade, works devoted to the development of electrochemical devices suitable for the detection of pesticides have gained growing interest as innovative alternative in terms of on-site detection, sensitivity, rapid response, miniature size, and low cost. Hence clay modified electrodes (CME) were applied for the electrochemical analysis of pollutants or drugs [1]. For instance, organic molecules bearing reducible aromatic nitro group have been detected at CME by means of adsorption stripping technique associated with differential pulse voltammetry (DVP) or square wave voltammetry (SWV). Carbon paste electrodes (CPE) containing clays were used for the electrochemical detection of nitrophenol [2], nifedipine, nimodipine drugs [3] and dinoseb, dinoterb herbicides [4]. Compared with a bare CPE, a significant improvement was observed in sensitivity by using clay-CPE. Methyl parathion, another pesticide, was also detected at a montmorillonite/carboxy cellulose composite modified electrode [5]. The presence of a surfactant, cetyltrimethylammonium bromide (CTAB), in the electrolyte solution enhanced the current response leading to a limit of detection down to 7×10^{-8} M. Moreover, organoclays, easily prepared by ion-exchange reaction with alkylammonium cations, are useful for the removal of environmental pollutants such as pesticides or phenols [6,7]. Indeed by changing the clay properties from hydrophilic to hydrophobic by intercalation of surfactants, such organoclays are likely to adsorb neutral hydrophobic molecules by non-polar interaction. Recently, a gemini surfactant intercalated clay-modified electrode was also used for the electrochemical detection of methyl parathion with a detection limit of 7×10^{-8} M [8]. Similarly a glassy carbon electrode (GCE) modified with an anionic clay intercalated with dodecylsulfonate

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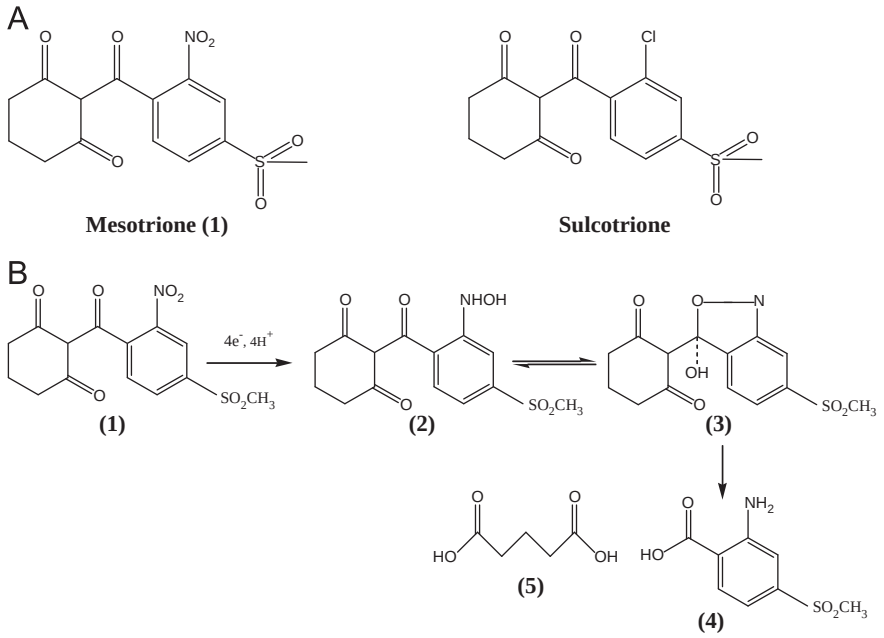
http://dx.doi.org/10.1016/j.talanta.2012.10.068



Scheme 1. (A) Mesotrione and sulcotrione formula. (B) Proposed electrochemical reduction pathway of mesotrione.

surfactant (MgAl-DDS) was used for the sensitive voltammetric determination of 2-nitrophenol [9].

Mesotrione (1) (Scheme 1A) is a recently marketed herbicide having an aromatic nitro group in its formula launched by Syngenta in European maize market under the brand name CALLISTO. Its quantification was generally reported using liquid chromatography tandem mass spectroscopy [10] or liquid chromatography coupled with fluorescence detection by an indirect method via the chemical transformation to the metabolite 2-amino-4-methylsulfonylbenzoic acid (AMBA) [11]. To our best knowledge, only one paper reports on the electrochemical analysis of mesotrione at hanging mercury drop electrode [12]. Using this method, a linear calibration curve was obtained in the range of 0.1–1.0 μM, with a limit of detection of 50 nM. This method is sensitive and relatively selective. However, because of the toxicity of mercury, future regulations may severely restrict its use in several measuring devices like mercury electrode. New alternative electrode materials are highly desired to develop 'environmentally friendly' stripping sensors. In the present work, we propose the use of organoclays as modifier of glassy carbon electrode for the electrochemical detection of mesotrione herbicide by square wave voltammetry.

2. Experimental part

2.1. Chemicals and reagents

Mesotrione, sulcotrione, cetyltrimethylammonium bromide (CTAB), didodecyldimethylammonium bromide (DDAB) and sodium nitrobenzenesulfonate (NaNBS) were purchased from Sigma-Aldrich. Acetate buffer solutions (0.1 M) were used as supporting electrolyte. All other reagents were of analytical grade and, all solutions were prepared with ultrapure water.

The clay mineral used in this study, namely Sa, was a smectite collected from Sabga (west-Cameroon, Central Africa). Its cationic exchange capacity, reported elsewhere, is 0.78 meq g^{-1} [13]. The clay was converted into the sodium form according to the procedure previously described [14]. Briefly, 1 g of the natural clay was stirred in 100 mL of 1 M NaCl solution for 14 h. The suspension was then centrifuged at 5000 rpm for 15 min, the solid sample was then stirred again in a fresh 0.1 M NaCl solution (100 mL) for 8 h. The solid was recovered by centrifugation and washed several times with distilled water until a negative test for chloride ions was achieved (titration with $AgNO_3$). The clay (SaNa) was dried at 40 °C for 24 h. Organoclays (SaCTA and SaDDA) were prepared by cationic exchange reaction. Namely, 1 g of SaNa was dispersed in 500 mL water solution containing two CEC (1.56 mmol) of surfactants (CTAB or DDAB) and stirred at 50 °C for 24 h. After centrifugation, the solids were washed once with ethanol and three times with water, then dried at 40 °C for 12 h. Chemical composition of both sodium (SaNa) and organoclays (SaCTA and SaDDA) are given in Table 1.

Table 1
Elemental analysis of clay samples.

Component (%)	Clay		
	SaNa	SaCTA	SaDDA
SiO_2	61.78	59.69	59.08
Al_2O_3	16.76	15.70	15.77
Fe_2O_3	4.52	4.19	4.26
MgO	0.13	0.13	0.12
CaO	0.12	0.12	0.11
Na_2O	1.23	0.09	0.12
K_2O	0.25	0.25	0.24
TiO_2	0.21	0.19	0.19
MnO	0.01	0.01	0.01
P_2O_5	0.04	0.04	0.04
Total	85.03	80.36	79.90

2.2. Instrumentation

Powder X-ray diffraction patterns (XRD) of clay samples were recorded on a SIEMENS D501 diffractometer using CuKα radiation (λ=0.15415 nm) in the 2–70° 2θ range in steps of 0.04° for a period of 4 s. Samples were analyzed as powder and as oriented clay films prepared by drying 1 mL of suspension (5 mg/mL) on glass slides. Transmission FTIR (KBr pellet) spectra were recorded on a NICOLET 5700 (Thermo electron corporation) spectrometer. Elemental compositions of clays were determined by Inductively

Coupled Plasma Atomic Emission Spectrometry (ICP-AES) with a PERKIN-ELMER Optima 3000XL spectrometer. The amount of surfactants (CTA and DDA) intercalated in the clays was determined by using a total organic carbon analyzer SHIMADZU TOC-5050 A. Water content in clay samples was calculated from thermal gravimetry analysis (TGA) using a TG-DTA92 thermogravimetric analyzer in the temperature range of 25–1100 °C, with a heating rate of 5 °C/min under air flow in an alumina crucible. Surface area of clay samples was determined by N_2 adsorption/desorption experiments (BET). Nitrogen adsorption measurements were carried out with a Micromeritics ASAP 2020 surface area and porosity analyzer. Prior to analysis, all samples were pre-treated for 12 h at 150 °C under vacuum. The BET surface areas were determined for the low-pressure region ($p/p_0 < 0.26$). The mesopore volumes and pore size distributions were calculated using the BJH model.

The adsorption isotherms of mesotrione on three clay samples were measured at 20 °C using the batch equilibrium method. The suspensions were kept in a vessel with continuous stirring. To get a homogeneous dispersion, the 10 mg samples were dispersed in 10 mL of 0.1 M acetate buffer (pH 6) and stirred for 12 h in the presence of different concentrations of mesotrione ranging from 1.5×10^{-5} to 3×10^{-4} M. After a contact time of 12 h, the suspensions were centrifuged. The amount of mesotrione adsorbed by the clay samples (q_e) was determined from the difference between the initial (C_i) and the final equilibrium concentration (C_e) per gram of adsorbent. The amount of mesotrione present in the supernatant was measured by UV–vis spectroscopy at $\lambda = 256$ nm using a Evolution 500 UV-visible spectrophotometer (NICOLET).

Electrochemical experiments were carried out with potentiostat/galvanostat AUTOLAB PGSTAT100 (Ecochemie), using a single compartment three electrode cell. Electrode potentials were measured with respect to an aqueous saturated calomel electrode (SCE), a Pt wire was used as counter electrode and a glassy carbon disk (GCE) as working electrode ($A = 0.07$ cm^2). The clay modified electrodes were prepared as follows: the GCE was first polished with 0.05 μm alumina slurry paste and ultrasonically cleaned for 5 min in a 1/1 ethanol/H_2O mixture, then rinsed with water. Aliquots of 10 μL of a suspension containing appropriate amounts of the organoclay were deposited on the surface of GCE and dried for at least 4 h to ensure their complete drying before use. All electrochemical experiments were performed in 0.1 M acetate buffer solution degassed by bubbling with argon for 30 min before starting the measurements to avoid interference due to oxygen reduction. Mesotrione stripping analysis was carried out first by accumulation at open circuit potential by rotation of CME at 500 rpm for 2 min under argon bubbling, then the electrochemical response was recorded between −0.4 and −0.95 V/SCE in SWV. The SWV optimized parameters are frequency, 25 Hz; and potential amplitude, 20 mV.

An exhaustive electroreduction of mesotrione was carried out at −0.7 V for 6 h using a glassy carbon plate (2 cm^2) as working electrode and the electrolysis products were identified by HPLC-UV using a Agilent 1100 chromatograph. A reverse phase column (Zorbax Eclipse XDB-C18, 5 μm, 150 mm × 4.6 mm) was used with a flow rate of 1 mL/min and $\lambda = 254$ nm. The mobile phase was composed of acetonitrile (Solvent A) and acidified water (H_3PO_4, 0.01% v/v; pH 2.9) (Solvent B) in a gradient mode: 0–5 min 5%A; 5–30 min from 5 to 70% A (linear); 30–32 min from 70 to 95% A; 32–33 min from 95 to 5% A; 33–35 min 5%A.

3. Results and discussion

3.1. Physico-chemical characterization of SaNa

The elemental composition of SaNa is reported in Table 1. These data are very similar to those previously reported elsewhere [13]. One can notice the presence of large amounts of SiO_2, sodium cation and iron component. XRD analysis of SaNa powder shows a main phase with a d_{001} at low theta value (1.107 nm), characteristic of a smectite type clay, and also a secondary mineral phase identified as feldspath (f.sp) (Fig. 1A). XRD pattern recorded with oriented clay film allows the enhancement of the 001 reflection (Fig. 1B). Under this preferential orientation, a slight shift of the basal spacing (d_{001}) from 1.107 to 1.382 nm was observed for SaNa. This increase of interlayer spacing can be due to different hydration states depending on the drying condition. The identification of montmorillonite (mt) was confirmed by exposing a dried SaLi sample to ethylene glycol vapor. The expansion of the *d*-spacing from 1.382 nm to 1.872 nm due to the swelling property of the clay is characteristic of a smectite type clay (data not shown). Thermal analysis shows that the water percentage in SaNa was 5% (Table 2). The quantification of non-exchangeable cations Na^+, K^+ and Ca^{2+} (respectively 0.0034, 0.0052 and 0.0020 per atom of Si in SaCTAB and SaDDA) compared to 0.0385 Na^+ per Si in SaNa confirms the presence of feldspath phases ($NaAlSi_3O_8$, $KAlSi_3O_8$, $CaAl_2Si_2O_8$) in the sample (Table 1).

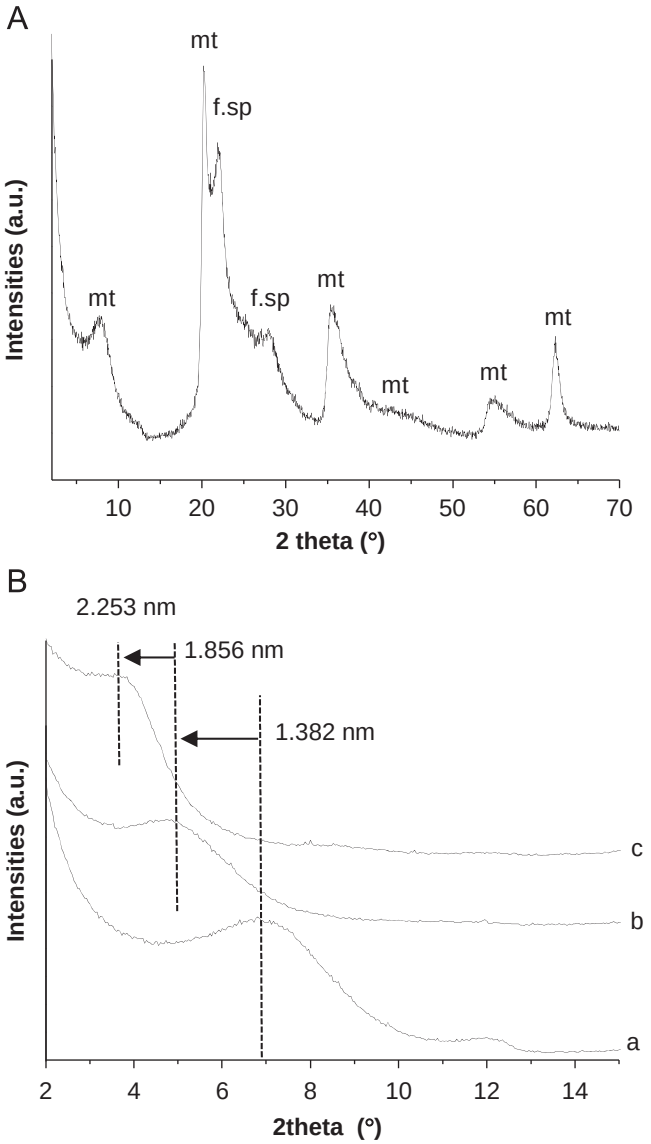


Fig. 1. (A) Powder X-ray diffraction pattern of SaNa with the corresponding attributions (mt) montmorillonite ($d = 11.07, 4.4, 2.14, 2.54, 1.67, 1.49$ Å) and (f.sp) feldspath ($d = 4.06, 3.2$ Å).(B) X-ray diffraction patterns of (a) SaNa, (b) SaCTA, (c) SaDDA samples prepared as films on glass plates.

Table 2
Physical characterization of studied clays.

Clay	d spacing* (nm)	Amount of surfactant (mmol/100 g clay)	BET surface area (m^2/g)	Total porevolume (cm^3/g)	Water content (TGA) (%)
SaNa	1.382	–	86	0.1574	5.53
SaCTA	1.856	50.2	28	0.0841	2.96
SaDDA	2.253	49.7	16	0.0609	2.22

* Oriented film coatings.

Cation exchange capacity (c.e.c.) was then determined to be equal to 85.25 meq/100 g of sample, a value quite close to that previously reported [13].

The nitrogen adsorption–desorption isotherm of SaNa (data not shown) displays a large hysteresis loop typical of mesoporous solids, as previously reported in the literature [13]. The specific surface area (86 m^2/g) and the pore volume (0.1574 cm^3/g) are relatively low (Table 2) due to high aggregation properties of nanoplatelets.

3.2. Physico-chemical characterization of SaCTA and SaDDA

The amount of organic surfactants (0.50 mmol/g) in the exchanged clays was calculated from carbon content of the samples, after subtraction of the carbon content of pristine clay (SaNa) (Table 2). The replacement of exchangeable cations (Na^+) by quaternary ammonium cations is confirmed by elemental analysis (Table 1).

XRD patterns of the organoclays prepared as thin films are illustrated in Fig. 1B and the corresponding basal spacings are given in Table 2. The intercalation of surfactants in between the clay layers is confirmed by the shift of the 001 series to low 2θ values. The d_{001} value is 1.842 nm for SaCTA which agree well with those of mt-CTA reported in the literature, suggesting a densely packed bilayer of organic molecules in the interlayer space [6,15,16]. For SaDDA, the value is slightly higher (2.232 nm) and corresponds also to that reported for mt-DDA [17].

FTIR spectra of the organoclay samples with those of SaNa and pure organic molecules are presented in Fig. 2. Large bands at 400–680 cm^{-1} and 980–1240 cm^{-1} correspond to the lattice vibrations respectively ν_{Al-O} and ν_{Fe-O} (Al/Fe–O_6 octahedra) and ν_{Si-O} (SiO_4 tetrahedra). The appearance of new peaks in the spectra of SaCTA and SaDDA samples compared to that of SaNa provides further evidence for the presence of surfactants in the exchanged clay samples. Both organoclays display characteristic vibrations bands at c.a. 2921 and 2850 cm^{-1}. These two peaks correspond to the asymmetric and symmetric CH_2 stretching modes of amine [15]. The vibration band related to the H–O–H bending at 1628 cm^{-1} seems to vanish in the spectra of organoclays. The hydrophobic character of these samples is confirmed by the lowering of water content (i.e. 55–40%) compared to SaNa (Table 2). Both specific surface area and pore volume were substantially reduced for SaCTA and SaDDA samples (Table 2).

3.3. Adsorption of mesotrione of clay samples

Organoclays have a strong capacity to sorb non-ionic compounds from aqueous solutions. Groisman et al. suggest that quaternary ammonium organoclays may be divided into two groups depending on the alkyl chain length. Organoclays containing short-chain quaternary ammonium ions, such as tetramethylammonium, are characterized by Langmuir-type isotherms associated with specific sorption sites. Clays exchanged with long chain quaternary ammonium, such as CTA and DDA, are called

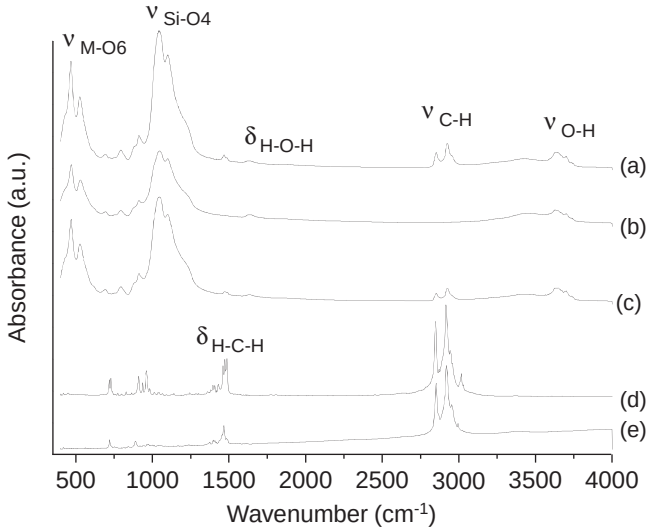


Fig. 2. FTIR spectra of (a) SaNa, (b) SaCTA, (c) SaDDA, (d) CTAB, (e) DDAB.

organophilic organoclays, they are generally characterized by linear isotherms over a wide range of solute concentrations [18]. Following their hypothesis, compounds with low or medium hydrophobicities would be more strongly sorbed on short-chain organoclay, whereas the more hydrophobic compounds would better sorbed on the long chain organoclay.

Adsorption isotherms were obtained by plotting q_e (mg g^{-1}) solid-phase concentration versus C_e (mg L^{-1}) liquid-phase concentration at adsorption equilibrium. The adsorption isotherms of mesotrione onto the three clays samples are compared in Fig. 3A. In all cases, after a strong increase of the adsorbed concentration versus the equilibrium concentration, q_e reached a plateau characteristic of the saturation of the surface by the pesticide (mesotrione). Surface saturation is reached at 3.99 mg/g, 5.80 mg/g, 22.14 mg/g, respectively, for SaNa, SaCTA and SaDDA. It clearly appears that modification of clay by organic surfactant molecules generates an increase in the adsorption properties of the clay. This effect can be attributed to a change of the nature of the mineral surface from hydrophilic to hydrophobic, increasing its affinity for the organic pesticide mesotrione. This phenomenon is more noticeable with SaDDA which has the highest adsorption capacity. The adsorption capacity of SaDDA for another pesticide, sulcotrione, was also studied (Fig. 3B) and the result will be discussed below.

3.4. Electrochemical study

3.4.1. Electrochemical behavior of mesotrione on GCE

Erdoğdu and Titretir have shown that nitro group of mesotrione can be reduced at hanging drop electrode [12]. This pesticide can be also reduced at a bare glassy carbon electrode (GCE) as shown in the cyclic voltammogram recorded under argon atmosphere to avoid interference with oxygen reduction (Fig. 4). An irreversible cathodic peak is observed at c.a. −0.75 V and the peak current intensity varies with the square root of the scan rate, showing that electrochemical reduction involves diffusion controlled electron transfer. The observed electrochemical response using CV seems to be consistent with a four-electron irreversible reduction of the nitro group (–NO_2) to hydroxylamine group (–NHOH) [19]. However linear sweep voltammetry as a function of rotation rate revealed that the number of electrons transferred is around 1.5 which suggests that the four electron reduction to hydroxylamine was not achieved or that the electroreduction at glassy carbon electrode was disturbed by electrode

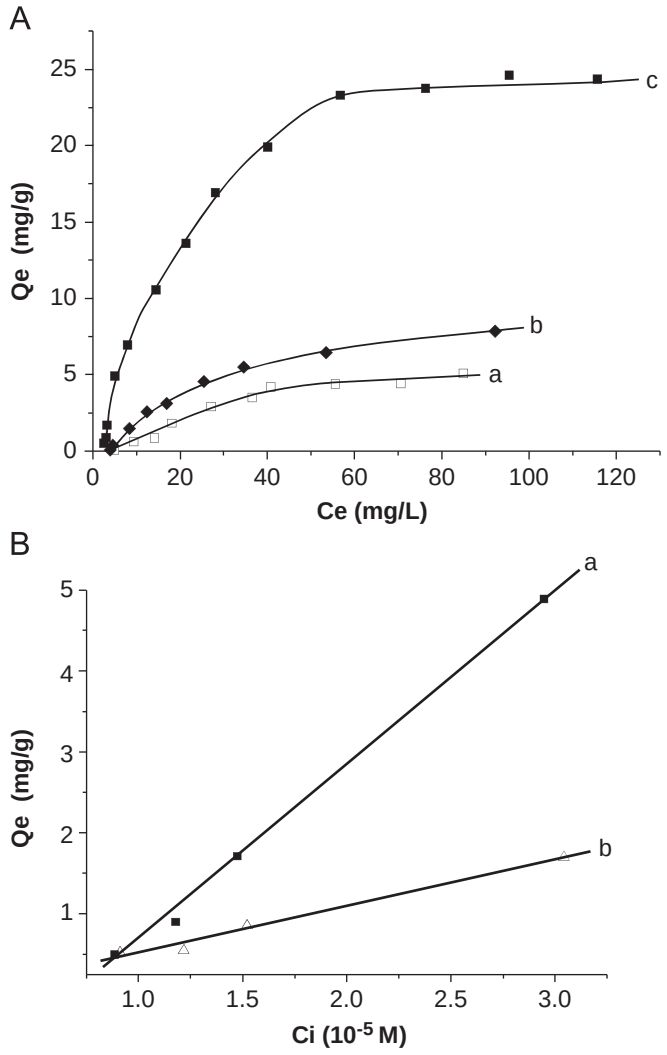


Fig. 3. (A) Adsorption isotherms of mesotrione on (a) SaNa. (b) SaCTA. (c) SaDDA. (B) Comparison of adsorption capacity (Q_e) as function of initial concentration (C_i) of (a) mesotrione and (b) sulcotrione on SaDDA.

passivation. In order to clarify the reduction mechanism, an exhaustive electrolysis of 5×10^{-5} M mesotrione solution was carried out at −0.7 V. The reduction products were identified in HPLC by comparison with metabolites formed in the biotransformation of the mesotrione by the bacterial strain *Bacillus* sp. 3B6 [20,21]. The presence of some unreduced mesotrione among electrolysis products confirms that the electrolysis was not total with only $3e^-$/mole, instead of the theoretical $4e^-$/mole (Scheme 1). As expected, the main reduction product was hydroxylamine (**2**) but two other by-products were also detected: an isoxazol-3-ol derivative (**3**) and the 2-amino-4-methylsulfonylbenzoic acid (AMBA, **4**). Indeed, a cyclized form of the hydroxylamine, isoxazol-3-ol moiety (**3**) is due to the intramolecular nucleophilic attack of the hydroxyl moiety on the carbonyl group. The isoxazol-3-ol derivative (**3**) is unstable, and slowly decomposed into 2-amino-4-methylsulfonylbenzoic acid (AMBA, **4**) and glutaric acid (**5**) (Scheme 1) as shown previously [21].

3.4.2. Electrochemical behavior of mesotrione on organoclay modified electrodes

Chemically modified electrode with clays or organoclays have been extensively explored for the electrochemical analysis of cationic species but also of neutral molecules, leading generally to an enhancement of current responses [1]. The electrochemical reduction of mesotrione was therefore examined at bare GCE, SaNa, SaCTA and SaDDA clay modified electrodes using square wave voltammetry (SWV) (Fig. 5). Indeed, SWV analysis is more sensitive than other electrochemical techniques. Compared to the signal obtained at GCE, the reduction peak is shifted towards less cathodic potential and the current peak intensity is largely enhanced at clay modified electrodes. Indeed, a well-defined reduction peak is observed for 2×10^{-5} M mesotrione at SaNa modified electrode (curve b), whereas it is quasi no observable at a bare electrode (curve a). Curves c and d in Fig. 5 correspond to the electrochemical reduction at SaCTA and SaDDA-CME. The current peaks are remarkably higher than with SaNa-CME, the signal was multiplied by 4 or 10 for SaCTA and SaDDA-CME, respectively. The current response depends on adsorption ability of these organoclays (vide supra) and the SaDDA-CME appears to be the best electrode for the electroanalysis of mesotrione.

3.4.3. Optimized mesotrione detection

This organoclay (SaDDA) was therefore used to optimize the experimental conditions required for the electrochemical detection of mesotrione. For all these experiments the mesotrione

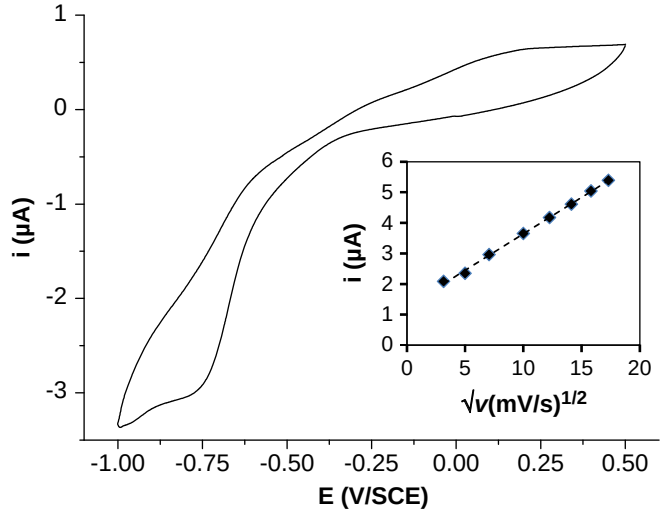


Fig. 4. Cyclic voltammogram of 1×10^{-4} M mesotrione at GCE (0.1 M AcBS pH 6. ν=10 mV/s). Inset shows the variation of Ip_c as a function of $\sqrt{\nu}$.

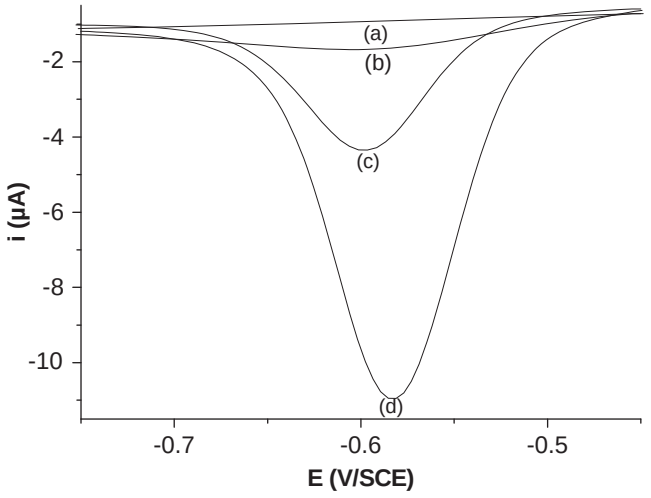


Fig. 5. Square wave voltammetry of 2×10^{-5} M mesotrione recorded at (a) bare GCE, (b) SaNa (c) SaCTA, and (d) SaDDA CME (0.1 M AcBS pH 6).

concentration was fixed at 2×10^{-5} M (see Supporting Information Fig. S1). The dependence of peak current on the accumulation time was studied under open circuit condition. A sharp increasing peak current was observed after 30 s to reach rapidly a plateau for time >60 s (see Supporting Information Fig. S1A). An accumulation time of 2 min was chosen for further analytical studies. The amount of organoclay coated on the electrode surface is expected to affect the electrode response. Different amounts of SaDDA, namely 10, 15, 20, 25 and 30 μg, were used to modify the carbon surface (see Supporting Information Fig. S1B). It appears that the highest current was obtained for 20 μg, a subsequent increase of the film thickness renders the mass transfer through the clay film more difficult. The same clay amount (20 μg) was therefore fixed for all experiments. The pH of the electrolyte solution is a critical factor affecting the electrochemical mechanism. As the pH decreases, the peak potential shifts towards more cathodic values with a slope of 40 mV/pH unit (see Supporting Information Fig. S1C). This value is lower to the expected value of 56 mV/pH, however it is close to the 35 mV/pH unit reported for the reduction of nitrobenzene in CTAB micellar medium [19]. Indeed, one can believe that the same electron transfer mechanism can be proposed for mesotrione reduction than for the electrochemical reduction of nitrobenzene on GCE in the presence of CTAB. The latter corresponds to a one step process involving four electrons and four protons but with a slowdown of protonation rate [19]. It should be noted that a slope of 57 mV/pH unit was found at SaNa CME (data not shown). In both cases, the current peak is maximum at pH 6.0, this pH value was chosen as the optimal for the detection of mesotrione and used for further experiments (see Supporting Information Fig. S1D). Similarly, a maximum response was found around pH 7 for the voltammetric determination of mesotrione at hanging mercury drop electrode [12].

As shown in Fig. 6, the current response depends on mesotrione concentration. The peak current intensity, measured from an extrapolated base line, increased with an increase in mesotrione concentration and the calibration parameters indicate a good fit to the linear model for a dynamic concentration range between 0.25 and 2.5 μM (Table 3). For higher concentrations, the current response reached progressively a plateau. The reproducibility of electrode fabrication was tested with five different SaDDA-CME prepared using the same procedure (20 μg). The calibration curves have an average sensitivity of 6.54 ± 0.31 A M^{-1} cm^{-2} (RSD=3%). A detection limit of 0.26 μM was estimated by the Clayton's method ($p=0.05$) [22]. Repeatability of current response was examined using the same SaDDA-CME for five independent current measurements in 2×10^{-5} M mesotrione, an electrode regeneration was made between each experiment by continuous cycling for 10 scans the CME in pristine buffer solution. A continuous decrease of the current response is observed (see Supporting Information Fig. S2), suggesting that the regeneration of the electrode was not enough efficient and therefore single-use electrodes should be recommended. However, it is not a limitation since these clay materials are not expensive and the fabrication process is reproducible (3%). Mesotrione determination was performed under these optimized conditions for three types of clays. Calibration parameters listed in Table 3 confirm that SaDDA modified electrode gives the best response.

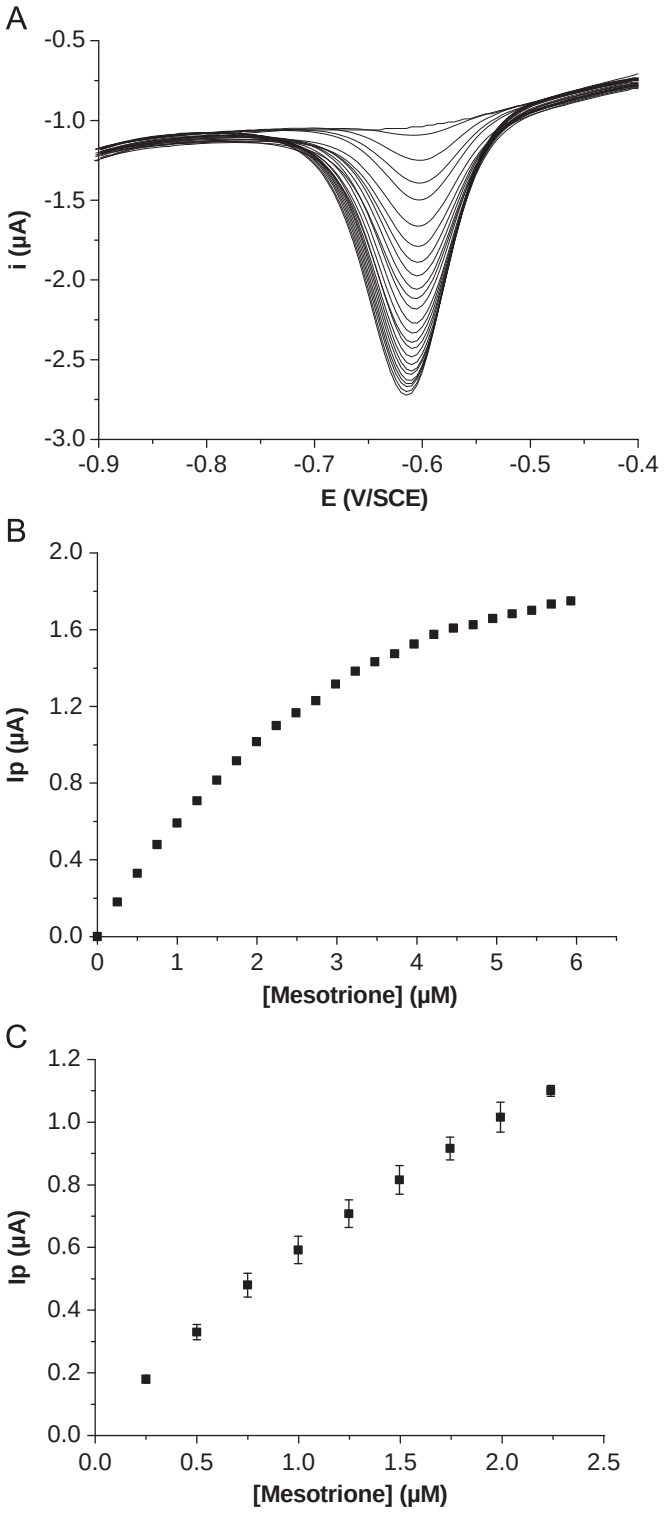


Fig. 6. (A) Evolution of current peak intensities as a function of mesotrione additions from 0 to 6 μM by 0.25 μM step at SaDDA CME. (B) and (C) the corresponding calibration curves (0.1 M AcBS pH 6).

3.4.4. *Interference study and medium effect*

The electrochemical response of mesotrione in the presence of possible interferents was also studied by SWV under the optimized conditions. Sulcotrione, an herbicide belonging to the triketone class and used in corn production, was chosen as a possible interferent. Its chemical formula is similar to that of mesotrione with the replacement of nitro group by a chloride atom (Scheme 1). Though it is not electroactive in the investigated potential range, a competitive accumulation may happen at the CME disturbing consequently the mesotrione determination. Mesotrione analysis was carried out in the presence of 1×10^{-5} M sulcotrione dissolved in the electrolyte solution. The base line confirms that sulcotrione is not reducible in the investigated potential range. The mesotrione calibration parameters determined in the presence of sulcotrione

Table 3
Calibration parameters at clay modified electrodes.in 0.1 M AcBS (pH 6.0).

Analyte	Clay	Condition	Sensitivity (A/M cm^2)	Concentration range (μM)	R^2 (n)
Mesotrione	SaNa	Pure water	0.13	5–19	0.9983 (7)
	SaCTA		1.58	1.25–9.80	0.9915 (8)
	SaDDA		6.54	0.25–2.24	0.9924 (9)
	SaDDA	+ Sulcotrione (1×10^{-5} M)	5.00	0.25–2.50	0.9988 (10)
		Volvic mineral water	6.28	0.25–2.50	0.9972 (10)
		Tap water	2.43	0.25–2.50	0.9988 (10)
CALLISTO		Pure water	4.56	0.25–2.24	0.9988 (10)
Nitrobenzene-sulfonate		Pure water	26.81	0.13–1.37	0.9988 (11)

(1×10^{-5} M) are reported in Table 3. A slight decrease in sensitivity was observed probably due to some adsorption competition between mesotrione and sulcotrione. However, the comparison of their respective isotherms shows that in the analysed concentration range, adsorption of mesotrione is stronger than adsorption of sulcotrione on SaDDA (Fig. 3B). Indeed, mesotrione is more hydrophobic than sulcotrione with an octanol/water partition coefficient (log P) of 0.11 compared to that of sulcotrione (−1.7) at pH 7. It was also possible to establish a calibration curve for the commercial form of mesotrione (CALLISTO). The resulting sensitivity was slightly lower (Table 3), probably due to the presence of excipients in the formulation that may disturb the adsorbability of mesotrione in clays. Mesotrione determination was also realized in real water samples (Volvic mineral water and tap water) (Table 3). In the latter case, the sensitivity decreases significantly.

3.4.5. Electrochemical behavior of 3-nitrobenzene sulfonate

As reported in the introduction, organoclay modified electrodes are quite efficient for the determination of nitro-compounds. In the present work, we have also quantified the sodium 3-nitrobenzene sulfonate (NaNBS) at SaDDA modified electrode. In the same stripping conditions and concentration range than previously used for mesotrione, the reduction peak of NBS was situated at the same potential (−0.62 V) but its intensity was higher (see Supporting Information Fig. S3). As a comparison, the calibration parameters of NaNBS are summarized in Table 3. The sensitivity is four times higher but the dynamic concentration range is smaller. Indeed, this molecule is hydrophilic with a calculated log *P* of −3.13 but it bears an anionic sulfonate group that would modify the interaction with SaDDA. This experiment illustrates the possibility to use SaDDA for the determination of other nitro-aromatic compounds.

4. Conclusion

Organoclays can effectively be prepared by an ion exchange of a natural Cameroonian smectite-type clay (Sa) with alkylammonium surfactants, modifying significantly their adsorption properties. A considerable increase was observed in the adsorption efficiency with SaDDA sample. The proposed sensor based on SaDDA modified electrode consists in an interesting alternative for the electrochemical analysis of mesotrione at hanging mercury drop electrode. The possibility of preconcentrating other organic pollutants, such as nitrobenzene or nitrophenol, makes this modified electrode promising for further development of warming sensors.

Acknowledgment

The authors thank Dr. Gilles Mailhot from ICCF to set up the Total Carbon Analysis and Dr. Franck Charmantray for his help in statistical treatment of data.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2012.10.068.

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