



SWV determination of glyphosate in Burkina Faso soils using carbon fiber microelectrode

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ABSTRACT

This paper presents an evaluation using carbon fiber microelectrode (CFME) for the determination of glyphosate in soils from Burkina Faso treated with Glyphonet SL 360 by square wave voltammetry (SWV). The maximum intensity of the electrochemical response signal of glyphosate has been optimized and conditions using a 0.2 M of phosphate buffer solution at pH 5.2 as supporting electrolyte and the SWV parameters frequency of 60 Hz, a scan increment of 10 mV and a pulse height of 60 mV. The limit of detection for glyphosate in the Glyphonet SL 360 formulation was $25 \mu\text{g L}^{-1}$ while the quantification limit was $83 \mu\text{g L}^{-1}$ with a linear dynamic range up to $50 \mu\text{g L}^{-1}$. In these conditions, a sequence of experiments led to recoveries in the range 88.5 to 102.3% for soil samples spiked with 50, 100 and $200 \mu\text{g L}^{-1}$ of glyphosate with a standard deviation of 11.5, 4.2 and 2.3% respectively indicating the precision of the method. The optimized method was successfully applied to determine the residues of glyphosate in soils collected in the fields in two different dates from the application period.

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INTRODUCTION

N-(phosphonomethyl) glycine, aka Glyphosate, is a nonselective herbicide and the most commonly used agricultural pesticide (Franz et al., 1997). This herbicide sale represents about 60% of the worldwide market of herbicides, totaling 1.2 billion dollars per year, making this product the non-selective herbicide most extensively applied, mainly due to its broad spectrum for the

elimination of weeds (Franz et al., 1997; Amarante et al., 2002).

The extensive use of this herbicide is worrying the environmentalists. Nevertheless, the environmental effects, as in the flora and thus in the microbiological soil population, are pernicious (Morrison et al., 1984; Bott et al., 2011; Haney et al., 2000). This situation is worsened due to its possible accumulation. Thus, Studies of the physicochemical

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properties of glyphosate, its interactions with water and soil components, as well as its extraction, detection and quantification in natural samples are necessary for a well-known of this component due to its effects on environment (Amarante et al., 2002; Pintado et al., 2012).

At the present, most studies for the analysis of glyphosate and its principal degradation product, aminomethylphosphonic acid (AMPA), make use of derivatization steps (Ibanez et al., 2006) or complex eluent like in ion exchange chromatography (European Commission, 2002).

Studies showed that glyphosate skeleton presents a secondary amino group that, when treated with nitrous acid is converted to an N-nitro group (Marsh et al., 1992). This one can be easily reduced; making some authors (Bronstad et al., 1976; Friestad et al., 1985; Moraes et al.; 2010) showed the possibility of applying differential pulse polarography (DPP) as an inexpensive and fast technique for glyphosate determination.

In the present work, the main objective is to develop and validate an electrochemical method for the determination of glyphosate formulated in Glyphonet SL360 in soils from Burkina Faso using carbon fiber microelectrodes based on square wave voltammetry. The optimization of the SWV voltammetric response in the glyphosate determination was carried out and compared with liquid chromatography using diode array detector, for the determination of glyphosate's residues in soils collected at the north-west of Burkina Faso.

MATERIALS AND METHODS

Reagents

Standard glyphosate (99.8%), AMPA (98%) and glyphonet 360 SL were received from DTE Datung Group. Acetic acid (99.8%), acetonitrile (CH_3CN) (99.9%), sodium chloride (NaCl) (99.5%), potassium dihydrogenophosphate (KH_2PO_4) (ACS reagent, 98%), potassium hydrogenophosphate (K_2HPO_4) (ACS reagent,

98%) and potassium hydroxide (KOH) (ACS reagent, 98%) were purchased from Sigma Aldrich.

Apparatus

Cyclic voltammetry (CV) and square wave voltammetry measurements were performed using an electrochemical analyzer PalmSens, (PalmSens Instrument, Netherlands) connected to a personal computer using Ivium PC and PSLite software. A three-electrode configuration was employed consisting of a carbon fiber microelectrode (12 μm diameter with a length of 5 mm) purchased from WPI, USA. The carbon electrode surface was renewed by a homemade electrochemical treatment. Indeed, the carbon fiber microelectrodes were first pretreated electrochemically in a mixture of sulfuric acid (0.5M)/ethanol (50/50 w/w) followed by a treatment in 0.2 M phosphate buffer solution using following conditions: potential scanning rate of 100 mVs^{-1} in the potential range -1.0 to 1.5 V vs Ag/AgCl (KCl 0.1 M) during 20 cycles. The quality of these microelectrodes was controlled by checking out of the $\text{Fe}(\text{CN})_6^{4-}$ electrochemical response as a probe. An Ag/AgCl (KCl 0.1 M) electrode was used as a reference and stainless wire as auxiliary electrode. Electrochemical experiments were carried out in a 10-mL glass voltammetric cell at room temperature. In this, 20 sensitive CFME were elaborated after the quality control for a complete investigation.

The comparative study was realized at the National Laboratory of Public Health (LNSP) using reverse phase HPLC with a high sensitivity diode array detector, and Agilent Zorbax chromatographic column with the following reference: Zorbax Eclipse XDB C18 4.6 x 250 mm, 5 μm of particles. The mobile phase was constituted of potassium dihydrogenophosphate/methanol at 96/4 ratio.

Solution preparation

A stock solution of glyphosate (1 g.L^{-1}) was prepared by dissolving the equivalent mass of glyphosate in acetonitrile. 0.2 M

phosphate buffer solution was used as the supporting electrolyte. The pH of the phosphate buffer solution was measured by a pH combined electrode and the exact value of pH was adjusted by addition of aqueous potassium hydroxide.

Experimental design and treatments

Tests in cotton and maize fields were conducted according to a simple block design on an area of 0.75 ha. The formulated glyphosate, Glyphonet SL 360, is applied on 0.5 ha and the untreated control plot is 0.25 ha. Tests on upland rice are conducted on an area. In this case, the untreated control plot is 0.15 ha. Glyphonet SL 360 is applied to soil in grassed or direct seeding after tillage. The dose used was 1080 g ha⁻¹ of Glyphonet, this according to the importance of weed.

Soil samples

Because glyphosate is strongly adsorbed to the soil surface by particles (Borggaard et al., 2008; Nicholls et al., 1991), we limited the research of glyphosate residues at the depth of 20 cm. According to a well established methodology for soils sampling (Reinaldo et al., 2008), 13 samples were taken in each field and mixed to form a composite sample. This composite sample was crushed and sieved through a sieve of 20 microns porosity according to a procedure described previously (Teofilo et al., 2008) and stored in the refrigerator at -20°C until analysis. In each case, a witness sample was taken before the application of herbicides in order to perform a physicochemical characterization of the different soils and to determine the state and the initial content of the residues of glyphosate soil prior to up tests.

An amount of 50 g of the composite soil was added to 125 mL of a 0.2 M KOH solution in a flask that was then closed and mechanically stirred for 15 min. All the volume was centrifuged during 15 min at 2000 rpm and the supernatant was transferred to a plastic flask. This operation was duplicated.

RESULTS AND DISCUSSION

Direct electrochemical detection of glyphosate

Figure 1 illustrates a SWV typical electrochemical response of glyphosate in acetate buffer solution at pH 5 using carbon fiber microelectrode. Indeed, as it is shown in this figure, a well defined redox peak appeared at - 875 mV versus Ag/AgCl/KCl 0.1 M and assigned to the reduction of acid group of glyphosate. This result is in agreement with previously reported works (Teofilo et al., 2008).

Recent studies (Sbai et al., 2007; Pontié et al., 2010) have demonstrated that CFME modified with combination of phthalocyanine and Nafion could be used without preelectrolysis step for the detection of methylparathion with a sensitivity of 20 nA L mg⁻¹ and a determination limit of 100 µg L⁻¹ under optimized SWV parameters. We previously demonstrated the possibility of carbon fiber microelectrode use, modified or not by tetrasulfonated nickel phthalocyanine to follow parathion methyl and its stable by-products such as p-nitrophenol (Tapsoba et al., 2009; 2012). In order to determine the most suitable conditions for glyphosate residues determination in soils based on carbon fiber microelectrode, we optimized the square wave voltammetry parameters.

Improvement of the sensitivity of carbon fiber microelectrode for glyphosate analysis

The electrochemical behavior of glyphosate on CFME was optimized in phosphate buffer solutions, the pH ranging from 2 to 11 by square wave voltammetry for the highest current intensity. Moreover, the square wave voltammetry parameters such as the frequency, the pulse height and the scan increment were also investigated for an optimum response of glyphosate using carbon fiber microelectrode.

Figure 2 shows the variation of the current intensity of the reduction peak of glyphosate with the pH value of the phosphate buffer solution. It is obvious through the

figure that the pH of the supporting electrolyte has a great effect on the efficiency of the electrochemical detection of glyphosate as it is reported elsewhere (Izutsu 2002; US EPA, 2006; Nicholls et al., 1991; Shifu et al., 2007). As it is illustrated on Figure 2, one can conclude that the highest current intensity corresponding to glyphosate reduction on carbon fiber microelectrode is obtained for a pH close to 7.2, suggesting that at this pH value, glyphosate is relatively stable and is probably on easily reducible form. These results are in good agreement with those reported in the literature indicating that glyphosate formulations are stable in water at pH 4-9 range at 35° C and stable for photodegradation in pH 5, 7 and 9 in buffered solutions under natural sunlight (Nicholls et al., 1991; Shifu et al., 2007). In addition, one could explain the low intensity at pH > 10.2, by a possible degradation of glyphosate that lowers its concentration in the buffer. At lower pH, one can observe a very low current intensity relative to the reduction of glyphosate. This behavior can be explained by a degradation of the glyphosate at low pH values and these obtained results are in agreement with those reported by Shifu et al. (2007) and Aquino et al. (2009)

Taking account of this optimal value of pH, we fixed the pH of the phosphate buffer solution at 5.2 while following the variation effects of the SWV parameters. The choice of this value is dictated by the soils acidity which is generally close to pH 5.

Figure 3 presents the frequency influence upon the SWV response in terms of stripping peak current. The plotting shows that the reduction peak current reaches a maximum at 60 Hz frequency which was adopted for all the following experiments.

In the case of scan increment and the pulse height, the investigations show that the best current intensity is obtained for a pulse height of 60 mV and a scan increment of 10 mV.

Thus, the further SWV experiments in this work were performed using a frequency

of 60 Hz, a scan increment of 10 mV, a pulse height respectively of 60 mV and a window potential ranging from -1.3 to 0 V. The phosphate buffer solution pH value is 5.2.

With the aforementioned optimum conditions, we established two calibration curves, in a different range of concentrations of Glyphonet SL 360, concentration range in a phosphate buffer solution at pH 5.2 using carbon fiber microelectrode as reported.

When recorded in the concentration range from 100 to 1000 $\mu\text{g L}^{-1}$ using the Glyphonet formulation SL 360, one can observe in Figure 4, the increase of the current intensity with the pesticide concentration. The linear regression is expressed in the following equation $I_p/\mu\text{A} = 0.0115 C + 7.4353$ ($R^2 = 0.98$) for the concentration up to 100 $\mu\text{g L}^{-1}$ with a standard deviation (SD) equal to 0.1.

Moreover, examination of the glyphosate reduction potential in Glyphonet SL 360 shows that its reduction potential shifts toward a more cathodic value by comparison with the value obtained when standard is used. Indeed, it evolves from - 830 mV to - 950 mV versus Ag/AgCl (KCl 0.1 M). This potential shift can be explained by the presence of different adjuvants in the formulation making glyphosate more difficult to reduce (Jones et al., 2007)

At lower concentrations, a straight line plotting of the current intensity versus glyphosate concentration in the range 50 - 150 $\mu\text{g L}^{-1}$ is obtained. The linearity of this representation is illustrated by the equation $I_p = 0.0006c + 0.0154$ ($R^2 = 0.9975$) with a SD of 0.005.

The limit of detection and the limit of quantification were estimated by using the following formula $\text{LOD} = 3*\text{SD}/m$, and the $\text{LOQ} = 10*\text{SD}/m$, where SD is the standard deviation and m the average of the slope of regression line according to Burgess (2000). The obtained value is equal to ca. 25 $\mu\text{g L}^{-1}$ and 83 $\mu\text{g L}^{-1}$ for LOD and LOQ, respectively. Compared with our work, Burgess et al (2000) obtained a LOD of 12 $\mu\text{g L}^{-1}$.

In previous work, Friestad and Brønstad (1985) reported an improvement to the first glyphosate determination method using polarography with detection and quantification limits of 500 and 1000 $\mu\text{g L}^{-1}$, respectively. In an earlier work using the SWV (Teofilo et al., 2004; Sato et al., 2001) a linear response range of 0.050 to 100.0 mg L^{-1} , detection and quantification limits of 25 and 80 $\mu\text{g L}^{-1}$, respectively, were obtained. Sato (2001) utilized anion-exchange chromatography with integrated pulsed amperometric detection (IPAD) and under optimized conditions; the detection limit was 50 $\mu\text{g L}^{-1}$ and the linearity range from 0.1 up to 50 mg L^{-1} . Thus, our work presents a great improvement in the determination of glyphosate by electrochemical techniques, principally by SWV using naked carbon fiber microelectrode without sample clean-up and derivatization. The detection limit of 25 $\mu\text{g L}^{-1}$ is better than the value obtained by chromatographic methods and comparable with the existing electrochemical techniques in the literature.

Analytical application for glyphosate determination in soils

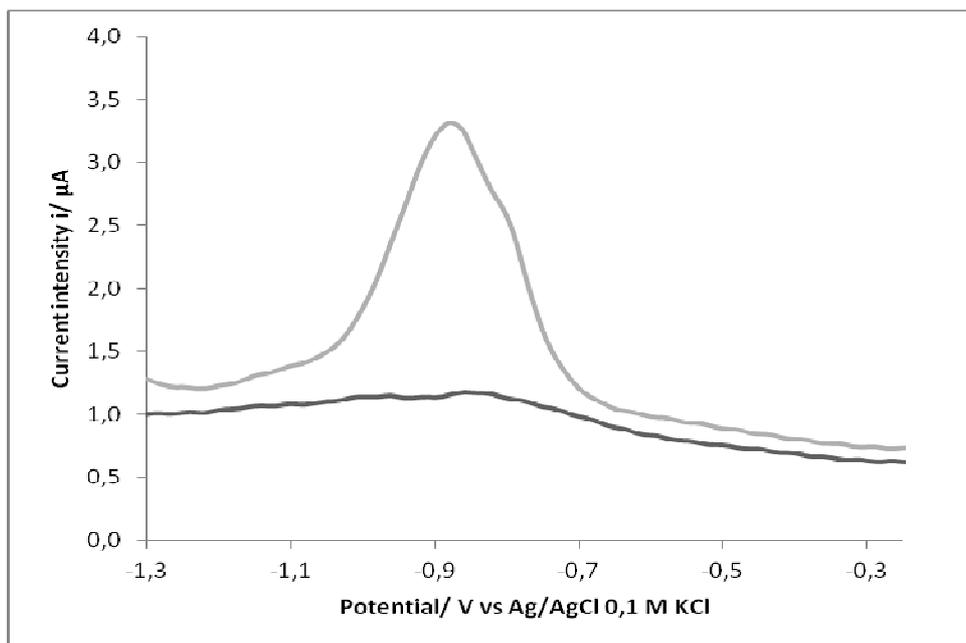
To validate this method, fortification experiments were performed using uncontaminated soil samples from the study area. A series of three (03) soil samples were spiked with Glyphonet SL 360 at concentrations level of 50, 100 and 200 $\mu\text{g L}^{-1}$. One sample without spiking was used as a blank. The glyphosate residues were analyzed in triplicate using the above optimized SWV conditions in pH 5.2 phosphate buffer solution. In order to compare the obtained results, the same samples were studied with validated reverse high performance liquid chromatography with a high sensitive diode array detector. The obtained results are reported in Table 1.

Table 1 shows glyphosate recovery from fortified soil samples. The results for these three samples indicate a reasonable precision due to complexity. The data are in

agreement with the literature ones which indicate that a validated method must have a recovery comprised between 70% and 120% (DG-SANCO, 2007).

In Table 2, we summarize the data obtained from the determination of the glyphosate residues in soils collected from the sites where Glyphonet SL 360 was applied. The samplings were realized on the first and the fifteenth day following the Glyphonet application.

As shown on Table 2, the amounts of glyphosate residues were determined according to the procedure described above in different soils after one and fifteen days following the treatment. One can see that the amounts of glyphosate in soils are important the day after application and this result is in agreement with reported work (Teofilo et al., 2008). The same analysis carried out 15 days post-treatment reveals the residual amounts of glyphosate residue are below LOD. These observations can be explained by a possible degradation of glyphosate, which could be influenced by the presence of some ions such as Fe^{3+} and Al^{3+} (Grunewald et al., 1998) on one hand and by the rainy season on the other hand. In order to confirm this hypothesis, we made a characterization of the different studied soils and the obtained results show that they are low in organic matter and phosphorus but rich in metallic cations like exchangeable aluminum and free iron which could accelerate the decomposition of glyphosate. Moreover, the analysis of groundwater shows two weeks after the application that the amount of glyphosate is lower than the detection limit. All these obtained data demonstrated the possibility to use of CFME for electrochemical analysis of glyphosate in soils as a low cost and sensitive method for glyphosate residue determination in soils and water.



Reference electrode: Ag/AgCl 0.1 M KCl. frequency F = 20 Hz; pulse height: 5 mV; scan increment: 20 mV.

Figure 1: Square wave voltammograms of phosphate buffer solution pH 5 (black) and 40 µg L⁻¹ of glyphosate (grey) using CFME ($\Phi = 12 \mu\text{m}$).

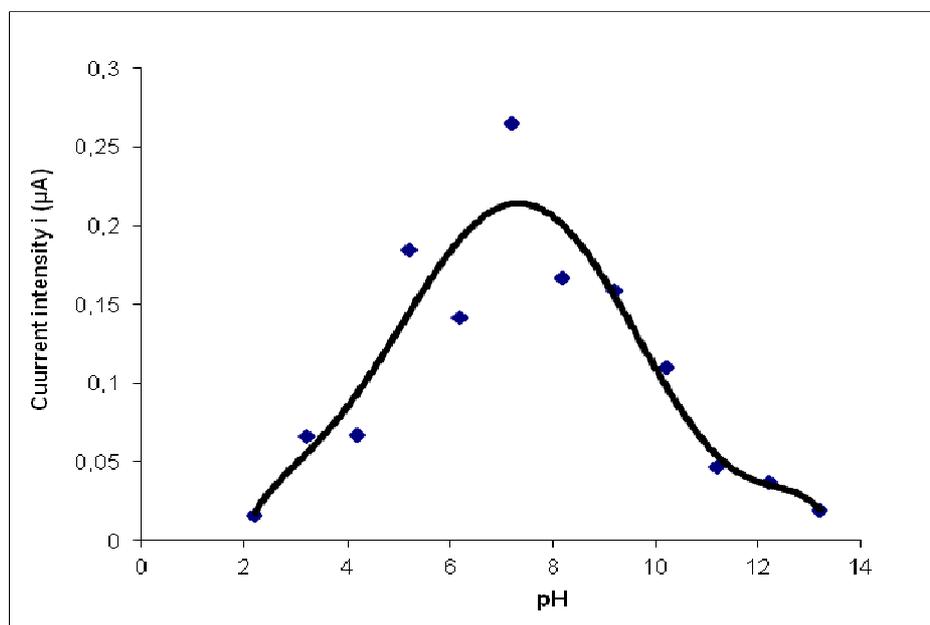


Figure 2: pH effect on the current intensity of the glyphosate reduction using CFME ($\Phi = 12 \mu\text{m}$). Reference electrode: Ag/AgCl 0.1 M KCl, frequency 10 Hz, scan increment: 5 mV and pulse height: 20 mV.

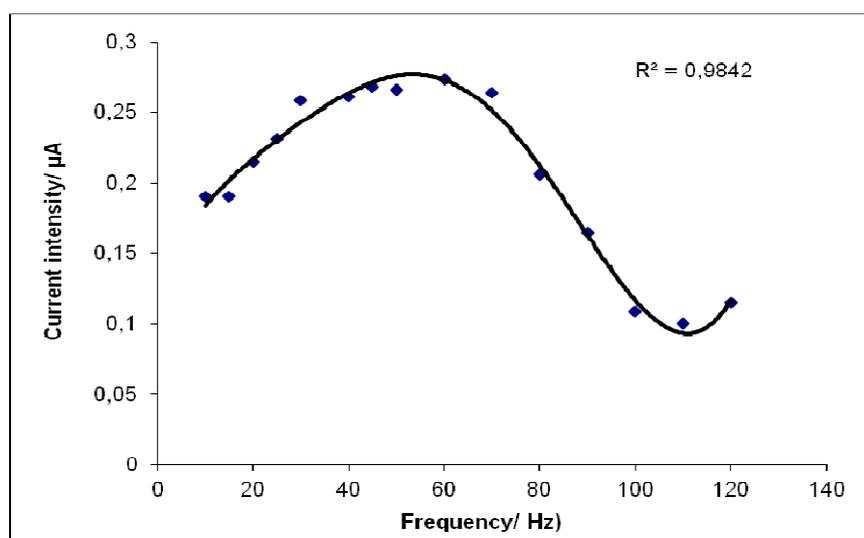


Figure 3: Evolution of the current intensity of the reduction of glyphosate with the frequency in pH. 5.2 phosphate buffer solution using carbon fiber microelectrode working electrode and an Ag/AgCl/KCl 0.1 M as reference electrode.

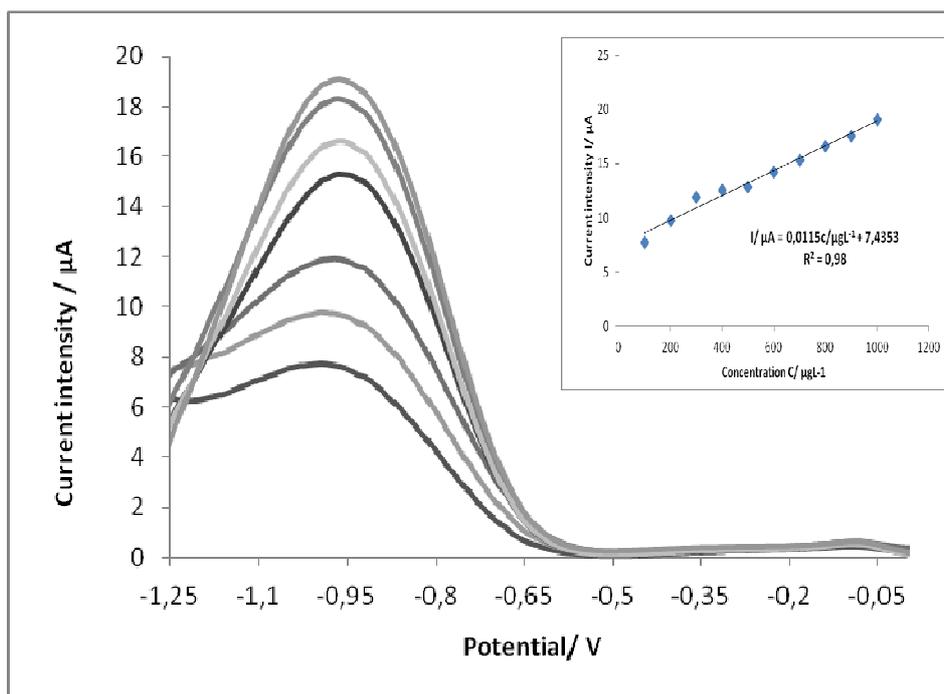


Figure 4: Analytical curves for glyphosate herbicide in Glyphonet SL 360 formulation determination in the concentration range of 100 to 1000 $\mu\text{g L}^{-1}$ in pH 5.2 phosphate buffer solution using carbon fiber microelectrode. Reference electrode: Ag/AgCl 0.1 M KCl. Frequency: 60 Hz. Scan increment: 10 mV. Pulse height: 60 mV.

Table 1: Glyphosate recovery from fortified soil samples.

| Sample number | HPLC-DAD | SWV | |
|---------------|------------------------------|---------|------|
| | Glyphosate mean recovery (%) | SWV SD% | |
| 1 | 90.3 | 88.5 | 11.5 |
| 2 | 93.6 | 95.8 | 4.2 |
| 3 | 99.3 | 102.3 | 2.3 |

Table 2: Glyphosate's residues determination in soil samples.

| Field # | Glyphosate quantification | Glyphosate quantification |
|---------|--|--|
| | $\mu\text{g kg}^{-1}$ of soil 1 day after | $\mu\text{g kg}^{-1}$ of soil 15 days after |
| 1 | 184.2 \pm 10.3 | < LOD |
| 2 | 183.3 \pm 9.6 | < LOD |
| 3 | 179.7 \pm 11.5 | < LOD |
| 4 | 152.5 \pm 12.1 | < LOD |
| 5 | 89.3 \pm 10.1 | < LOD |
| 6 | 106.6 \pm 11.3 | < LOD |

Conclusion

The present study reports, for the first time, the elaboration of a remarkably sensitive carbon fiber microelectrode (CFME) for glyphosate residues determination in soils treated by Glyphonet SL 360 formulation using square wave voltammetry. The best performances were obtained using SWV techniques with the following parameters: frequency 60 Hz, pulse height 60 mV and a scan increment 10 mV; thus a LOD of 25 $\mu\text{g L}^{-1}$ and a LOQ of 83 $\mu\text{g L}^{-1}$ are reached for soils spiked with glyphosate. These sensitive tools permit the determination of the residues of glyphosate in soils following its treatment by Glyphonet SL 360 formulation with a precision close to previous study but more efficient, sensitive and mainly low cost and rapid. In perspective, we will pursue this study by increasing the sensitivity of CFME using a surface modification as we reported recently (Tapsoba et al., 2009).

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