Electrochemical analysis of Fenuron herbicide by a carbon paste electrode modified by a functionalized NiAl-Layered Double Hydroxide

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Abstract

Environmental pollution by usage of pesticides as fenuron increases health risk, due to carcinogenic and teratogenic properties of these compounds. There are needs to develop a rapid and cheaper detection methods for quantification of fenuron. In this work, an inorganic-organic composite material was obtained by intercalation of sodium dioctylsulfosuccinate (DSS) within the interlayer space of a Nickel-Aluminum Layered Double Hydroxide (NiAl-LDH). The structure of the pristine LDH and the intercalated-LDH was confirmed using Fourier transform infrared spectroscopy, X-ray diffraction and thermal analysis. The modified LDH was used to elaborate an amperometric sensor for fenuron herbicide by differential pulse voltammetry (DPV) via a carbon paste electrode (CPE). The electrochemical procedure for fenuron analysis was based on the immersion of the working electrode in the electrolytic solution containing appropriate amount of herbicide, followed by voltammetry detection without any preconcentration step. The peak current obtained on the CPE modified by the organo-LDH was 2-fold higher in comparison with the pristine LDH/CPE. The observed increase in the signal of fenuron was attributed to the high organophilic character of this composite material induced by the modification using DSS. The effects of some experimental parameters (pH of medium and percentage of the modifier in the paste) on the stripping response were investigated in order to optimize the sensitivity of the organo-LDH modified electrode. Linear calibration curves were obtained in the fenuron concentration ranging from 0.5 to 1 μmol.L⁻¹ and 1 to 5 μmol.L⁻¹. The limit of detection (LOD) calculated on the basis of a signal-to-noise ratio of 3 was 1.8×10⁻⁹ mol.L⁻¹ (low concentration range) and the limit of quantification (LOQ) was 6×10⁻⁹ mol.L⁻¹. The interference effect of various inorganic ions likely to influence the stripping determination of the fenuron was also examined, and the applicability of the method was verified by the determination of fenuron in a river sample collected down-town Yaoundé.

Keywords: Anionic surfactant; Organo-LDH; Fenuron, Carbon paste modified electrode; Electroanalysis

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1-Introduction

Herbicides are frequently applied in the environment for pre and post-emergence weeds control. Large amounts are also used on non-cultivated areas such as roads and railways. Fenuron (1,1-dimethyl-3-phenylurea, referred as FEN hereafter) is one of the herbicides commonly used today [1]. This phenylurea herbicide is used to control the germination of broadleaf weeds and grasses [2]. Because of its widespread use and relatively long lifetime in the environment, its residues have been detected in ground and surface water [3,4]. These residues constitute a very serious environmental issue for human health and ecosystems, since FEN has been recognized to be toxic with mutagenicity and carcinogenicity issues [5,6]. Its accurate detection in the environment (soils, water and crops) is of critical importance in order to obtain the extent of contamination in a selected area and recommendations for necessary removal procedures. Several analytical techniques have been used for the analysis of phenylurea herbicide, mostly based on gas or liquid chromatography [7-9]. Although, these methods have been successfully employed, they require long analysis time and several pre-treatment steps. Also, some of them exhibit low sensitivity and selectivity. Thus, the developments of simple, low cost and sensitive alternatives for FEN detection are still needed.

Electroanalytical methods are very effective in the analysis of hazardous compounds such as pesticides (use for disease and control pests), particulary linked to environmental issues like water pollution. From literature works, different types of material have been successfully used as modifier of electrodes for the detection of pesticides in water, including titanium-dioxide nanoparticule and cetyltrimethylammonium bromide based carbon paste electrode [10] and tungsten oxide hydrates nanorod modified carbon paste electrode for detection of amitrole [11] and carbendazim [12]. Other well-known materials such as Layered Double Hydroxide (LDH) have been used as electrode modifier [13-15] for the
determination of environmental pollutants. In fact, LDHs form a class of synthetic layered metal hydroxide materials, with excess of positive charge in their brucite-like layers. These types of minerals have received considerable attention in sensing applications because of their biocompatibility and swelling properties [16,17]. Despite these attractive properties, LDHs exhibit poor selectivity and restricted adsorption capacities for hydrophobic organic compounds because of their hydrophilic surfaces [16-18]. In order to circumvent these weaknesses, functionalization of LDH with various organic and inorganic components had been recommended. Many works have been reported on the functionalization of LDH via the intercalation of organophilic anionic surfactants in the interlayer space [14,19,20]. The resulting materials displayed high affinity for hydrophobic contaminants [21], including phenylurea herbicides [22].

The development of electrochemical sensor for the determination of phenylurea has attracted an increasing interest in the few past years. In that context, Siara et al [23] developed a sensitive electrochemical method for quantifying linuron using zeolite modified carbon-paste electrode. Manisankar et al [24] elaborated a polypyrrole modified electrode for electrochemical determination of isoproturon. Also, Gonzalez de la Huebra et al [25] described the use of a carbon fiber microelectrode to evaluate the electrochemical behavior and electroanalytical determination of linuron in soil extracts. Recently, Wong et al [26], elaborated a nickel octylbutoxy-phthalocyanine complex to modify a carbon paste electrode for the sensitive and selective electroanalysis of diuron herbicide. However, among the wide range of phenylurea compounds, little works have been reported on the development of electrode for amperometric sensor quantification of FEN [27]. Therefore, there is need to develop low cost electrochemical sensors that could improve the analytical response of FEN and provide information concerning their detection. The use of an organo-LDH as electrode
modifier for the electroanalysis of phenylurea herbicides such as FEN has not yet been reported. Thus, the main intention of the current work is to develop an electrochemical method for FEN quantification based on a carbon paste electrode modified by an organo-LDH. Thus, a nickel-aluminum based LDH (NiAl-LDH) was synthesized and modified with the organophilic anionic surfactant sodium dioctyl sulfosuccinate (DSS). Due to the sorbent properties of organo-LDH towards FEN (hydrophobic interaction), its good application as electrode modifier was also expected toward the detection of FEN. The proposed sensor manifested the applications of detection of FEN in water sample.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade, and used as received. FEN (98.7%) was purchased from Prolabo. A stock solution of FEN (0.01 M) was prepared in ethanol (95%). Sodium dioctylsulfosuccinate (DSS) from Prolabo was used as received, while the acetate buffer solution used as supporting electrolyte was prepared by mixing 0.1 M CH$_3$COONa and CH$_3$COOH (Riedel-de-Haën). Al(NO$_3$)$_3$ and Ni(NO$_3$)$_2$ were purchased from Sigma Aldrich. Methylparathion was purchased from Supelco, and a stock solution (0.01 mol.L$^{-1}$) was prepared in ethanol. Glyphosate was purchased from Sigma Aldrich and a stock solution (0.01 mol.L$^{-1}$) was prepared in deionized water. CaCl$_2$, MgSO$_4$, NaCl, PbCl$_2$ and ZnCl$_2$ (from sigma Aldrich) were used to prepare solution for interferences studies. The pH was adjusted by aliquots of NaOH and HCl (37%) purchased respectively from BDH and Prolabo. All the aqueous solutions were prepared using deionized water.
2.2. Preparation of LDH and modified LDH

NiAl-LDH was prepared by coprecipitation method using an experimental procedure recently reported by Kameni et al [20]. In a typical experiment 50 mL of a mixed salt solution containing Al(NO$_3$)$_3$ (45 mmol) and Ni(NO$_3$)$_2$ (15 mmol) were prepared in deionized water previously boiled, and the mixture was purged with N$_2$ to avoid carbon dioxide. Then, 25 mL of sodium hydroxide (2 M) was added dropwise to the solution, under vigorous stirring. The pH was maintained at 10.1 ± 0.5 during the addition of the NaOH solution. The solid product formed was recovered by centrifugation, thoroughly washed with deionized water and oven-dried at 70°C for 24 hours. The resulting material prepared was labeled NiAl-LDH.

The synthesis of organo-LDH (named NiAl-DSS) was performed using the homogeneous co-precipitation method adapted from method reported in the literature for the synthesis of modified LDH [28]. Practically, three solutions were prepared using freshly boiled deionized water. One of 50 mL containing a mixture of nickel nitrate 0.045 mol and aluminum nitrate 0.015 mol, and other one involving 10 mL of 0.001 M of modified agent (DSS) and the last one of 25 mL of sodium hydroxide 2 M. These solutions were concomitantly added dropwise into a round bottom flask under stirring and under nitrogen atmosphere. The pH of the mixture was kept between 9.5 and 10.5. Once the addition was completed, the resulting suspension was vigorously stirred under nitrogen atmosphere at 75°C for 16 hours. Afterwards it was filtered and the solid product intensively washed with deionized water and dried in an oven at 70°C for 24 hours.
2.3. Characterization

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, \(\lambda = 1.54056 \text{ Å}\)).

Thermogravimetric analysis of samples were carried out under nitrogen flow (25 mL.min\(^{-1}\)) using a TA instrument Q5000. About 20 mg of powder sample was placed on the thermobalance of analyzer, which was purged with helium gas. The measurements were recorded between 50-800°C with a temperature ramp of 10°C min\(^{-1}\), data analysis was performed using universal analysis 2000 software package. On each plot, the results were presented by the Thermal Gravimetric (T.G) weight loss curve, and the first derivative of derivative of this curve (D.T.G).

FTIR spectra were recorded using Alpha spectrometer from Bruker Optics using the KBr method in the spectral range from 4000 to 500 cm\(^{-1}\). The spectra resolution was 4 cm\(^{-1}\).

2.4. Working electrode preparation, electrochemical equipment and procedures

Carbon Paste Electrodes (CPEs) were prepared by mixing carbon powder (particle size < 325 mesh), pasting liquid (mineral oil) and LDH or organo-LDH particles in the weight ratio 60:30:10. The modified and unmodified paste electrodes were packed into teflon tubes (6 mm internal diameter), equipped with a stainless steel screw and piston acting as the electrical contact. The electrode surface was polished with filter paper prior to the experiment. The CPE/NiAl and CPE/NiAl-DSS were used as working electrodes in a three-
electrode cell configuration, with Pt wire as counter electrode while a saturated calomel electrode (SCE) served as reference electrode.

The electrochemical measurements were performed on a μ-Autolab potentiostat controlled by the GPES Electrochemical analysis system (Echo chemie, Holland) and connected to a computer. Cyclic voltammograms and differential pulse voltammograms (DPV) were recorded by immersing the working electrode in the electrolytic solution containing appropriate amount of FEN followed by voltammetry detection without any preconcentration step. Precisely, 25 mL of the supporting electrolyte was placed in the voltammetric cell and the required volume of FEN solution was added through micropipette to obtain the desired concentration of FEN. The solution was then de-aerated with nitrogen for 10 min after which, the voltammetric curve was recorded. Prior to the next measurement, the electrode was regenerated by transferring it to a blank acetate buffer solution under stirring, where the trace amounts of FEN totally desorbed after 1 min.

3. Results and discussions

3.1. Characterization of LDH and organo-LDH

The FT-IR spectra of NiAl and intercalated NiAl samples are displayed in Figure 1A. The broad band centered around 3415 cm⁻¹ in the spectrum of NiAl was attributed to the stretching vibration mode of hydroxyl group of LDH and water molecules (intercalated and physically adsorbed) [29]. The bending vibration of these water molecules is also reflected in the band at 1633 cm⁻¹. The band at 1333 cm⁻¹ was assigned to NO₃⁻ present in the interlayer space to compensate the cationic charge of the NiAl layers. The bands at 652 and 548 cm⁻¹ were attributed to metal-oxygen bond (Ni-O-H, Al-O-H and O-Ni-O, O-Al-O) generated by
various lattice vibrations [30,31]. The spectrum of NiAl-DSS showed new bands. The bands in the range 2849 cm$^{-1}$- 2981 cm$^{-1}$ were assigned to aliphatic C-H stretching vibration [32, 33]. The band at 1464 cm$^{-1}$ corresponds to the bending vibration of these aliphatic C-H bonds [31,34]. The band at 1729 cm$^{-1}$ indicated the presence of carbonyl group [32,35] and the band at 1207 cm$^{-1}$ is due to stretching vibration of O-CO-C [35]. The bands observed at 1159 and 1038 cm$^{-1}$ are due to the antisymmetric and symmetric stretching vibration of S=O [36]. These bands indicate the presence of DSS in the synthesized material. The band assigned to nitrate anions (at 1333 cm$^{-1}$) was not present. This result indicated that DSS represents the major anion present in the interlayer space of NiAl-DSS. The main features of FT-IR spectra of raw LDH and functionalized LDH are presented as supplementary material in Table SI 1 for band assignments.

The XRD pattern of the precursor material (NiAl) is shown in Figure 1B (a). The peaks at 11.4° and 22.8° (2θ) correspond to the (003) and (006) basal planes of the LDH respectively [37]. The NiAl d-spacing was 7.75 Å, which is in agreement with previous studies [38]. The presence of well-defined reflections (012), (110) and (113), indicates the good crystallinity of this material [21,39]. On the XRD pattern of NiAl-DSS, the characteristic peak of the (003) diffraction plane shifted to the small-angles, with a d$_{003}$ value of 27.03 Å. This corresponds to an increase of 19.28 Å indicating the important expansion of the interlayer space after intercalation of DSS (Figure 1B (b)). The molecule size of DSS ions was estimated using ChemSketch software, this was found to be approximately 22 Å (length) and 5 Å (width). If DSS ions are arranged vertically in the interlayer space of NiAl-DSS, then the theoretical value of the d-spacing after modification is expected to be 29.75Å (7.75 + 22 = 29.75 Å), while the experimental value obtained (27.03 Å) suggests a pseudo paraffin-type monomolecular arrangement of DSS ions in the interlayer of NiAl-DSS. Thus, from the
results of the XRD studies, it could be inferred that the DSS anions were successfully
intercalated into the LDH galleries.

The results of thermogravimetric analysis of NiAl and NiAl-DSS are presented in Figure 1C
(a and b). The TGA curve of NiAl (Figure 1C (a)) showed two decomposition steps. The first
step was observed between 25° and 170°C with a weight loss of 10% which corresponds to
the water molecules adsorbed on the external surface of NiAl or in the interlayer surface. The
second weigh loss observed between 250° and 500°C, is due to the dehydroxylation of the
metal hydroxide layer [40,41]. The thermal behaviour of NiAl-DSS (Figure 1C (b)) showed
multiple thermal events. In the temperature range of 50-150°C, organo-LDH display lower
weight loss than LDH (7%) indicative of less free water in their bulk structure probably due
to the hydrophobic nature of DSS. The mass losses at 244°C and 284°C (Figure 1D)
correspond to the decomposition of intercalated DSS [42]. The weight loss at 335 °C
corresponds to the dehydroxylation of NiAl [20].

(Figure 1 here)

3.2. Application for the electrochemical determination of Fenuron

3.2.1. Active surface area of the working electrode

The active surface area of electrodes was studied using Randles Sevcik equation [11].
Area was investigated utilizing cyclic voltammetric at different sweep rates using
K₃[Fe(CN)]₆ solution 10⁻⁴ M in NaCl solution 0.1. From the slope of the plot of Ip versus v½
(Figure SI 1), the A value was calculated using:

\[ i_p = (2.69 \times 10^5)n^{3/2}AD_R^{1/2}v^{1/2}C_o \]  
(Equation 1).
Where \( n \) is number of electron (\( n=1 \)) involved in the reaction, \( i_p \) indicated anodic peak current, \( D_R \) is diffusion coefficient (7.6\( \times \)10\(^{-6} \) cm\(^2\)/s [11]), \( A \) represents the working electrode surface area and \( v \) is the sweep rate while \( C_o \) is \( K_3[\text{Fe(CN)}_6] \) concentration 10\(^{-4} \) M. The calculated effective surface area were found to be 0.015 cm\(^2\) and 0.042 cm\(^2\) and 0.227 cm\(^2\) for bare CPE and with CPE/NiAl-LDH and CPE/NiAL-DSS respectively.

### 3.2.2. Fenuron behavior on modified electrodes

In order to study the electrochemical behaviour of FEN on the CPE modified with the organo-LDH, multicyclic voltammetry was conducted in 0.1 M acetate buffer. Prior to this, the effect of nature of electrolytic solution was examined. Thus, the electrochemical response of FEN was investigated on CPE/NiAl-DSS in 0.1 mol/L acetate buffer (pH 4.7) and 0.1 mol/L phosphate buffer (pH 5) solutions by cyclic voltammetry. The results is shown in Figure SI 2. In acetate buffer, the sensitivity is higher compared to the response obtained with phosphate buffer. Hence, all experiments were carried out in acetate buffer as supporting electrolyte.

Figure 2 presents the voltammograms of 50 µM of FEN on the bare CPE or CPE modified with either LDH or its organically modified form. On bare CPE (Figure 2a), the electrochemical response is made of two redox system: a irreversible anodic peak (\( E_a = 0.92 \) V) and a pair of reversible peaks (\( E_a = 0.68 \) V and \( E_c = 0.67 \) V). As one can notice during the first scan, one peak appears on the anodic sweep at 0.92 V, when the scan direction is inversed only one cathodic peak apper at 0.67 V. In the successive cycles a new anodic peak appear at 0.68 V on the anodic sweep, which form a reversible system. It should be noted that, after the first scan the intensity of peak current of the system which appear around 0.92 V decreases relatively slowly during the multi scan, suggesting a low passivation of the
electrode at this concentration [43]. The present of the reversible system which is centered at
0.675 V depend on the oxidation product of FEN, which appear at 0.92V. In fact, when the
potentials were scanned from 0.4V to 0.7V (Figure SI 3), the reversible redox system did not
appear. This reversible system could be due to the presence of quinonic function generated on
the aromatic ring after the first oxidation of FEN [43,44].

In order to compare the electrochemical behaviour of FEN on the CPE/NiAl and
CPE/NiAl-DSS, similar experimental procedure was used. As shown in Figure 2 (b and c),
the electrochemical behavior of FEN on the CPE/NiAl and CPE/NiAl-DSS was similar to
that recorded on the bare CPE. However, there are some remarkable differences:

- The voltammogram obtained on CPE/NiAl (Figure 2b) showed from the second scan,
a reduced shoulder peak which appears at 0.98 V, whose intensity increases with the
number of scans. This shoulder could be attributed to the reduction of degradation
product after oxidation of FEN.

- On the voltammogram obtained on CPE/NiAl-DSS (Figure 2c), the system which
appear around 0.68V on CPE/NiAl, shifts toward the cathodic potential for about 60
mV.

Compared to CPE/NiAl-DSS (Figure 2d), the signals recorded during the first scan on
bare CPE and CPE/NiAl are less intense. Indeed, the current associated to the oxidation of
FEN on CPE/NiAl-DSS was 2-fold and 2.7 fold more intense than that recorded on
CPE/NiAl, and CPE respectively. This effect was due to the presence of the organophilic
anionic surfactant in NiAl-DSS which improves substantially the affinity of the electrode
surface for FEN present in the analytical solution.
To yield more insights in the electrochemical behaviour of FEN on the CPE/NiAl-DSS, the effect of sweep rate on electrooxidation signal of FEN was explored using the voltammetry technique (Figure 3A) and voltammograms were recorded by varying the scan rate in the range 5 mV/s to 125 mV/s. An increase in anodic peak was observed with increasing scan rate. A plot of the anodic peak current versus the square root of \(v\) exhibits a linear dependence (Figure 3B). This result indicates that the charge transfer at the modified electrode is controlled by diffusion. We have also plotted \(\log i_p\) versus \(\log v\) for the oxidation peak (Figure 3C). This plot followed the equation \(\log i_p = 0.47535 \log v + 1.6591\). It is well known that, the slope with values of 0.5 indicates diffusion-controlled processes and slope with values of 1 indicated adsorption-based processes [45], intermediate values imply mixed processes. In this case, the slope value of 0.47 indicated that the oxidation of FEN occurring on the CPE/NiAl-DSS is mainly a diffusion controlled process [13]. We Also noticed that, the \(E_p\) of the oxidation peak was also dependent on the scan rate. The peak potential shifted to more positive values with increasing the scan rate. Further, \(E_p\) versus \(\log v\) is also linear (Figure 3D). The Laviron equation [46] was used to estimated \(\alpha n\) and \(K_s\) values as follows.

\[
E_p = E^0 + \left(\frac{2.303RT}{anF}\right) \log \left(\frac{RTK_s}{anF}\right) + \left(\frac{2.303}{anF}\right) \log v
\]  
(Equation 2).

Where \(\alpha\) is the electron transfer coefficient, \(K_s\) is the standard rate constant of the surface reaction, \(v\) is the scan rate, \(n\) is the electron transfer numbers and \(E^0\) is the formal potential. \(K_s\) and \(\alpha n\) values can be concludes from the intercept and slope of the linear plot of \(E_p\) with respect to \(\log v\), if the value of \(E^0\) is know. The \(E^0\) value at CPE/NiAl-DSS can be deduced from the intercept of \(E_p\) versus \(v\), curve by extrapolating to the vertical axis at \(v = 0\) (Figure SI 4). Knowing \(E^0\) and from the graphical representation of \(E_p\) versus \(\log v\), the values of \(\alpha n = 0.81794\) and \(K_s = 3.7 \times 10^3\ \text{s}^{-1}\) were obtained from the slope and intercept, respectively.
Since for a totally irreversible electron transfer $\alpha$ was assumed as 0.5, the $n$ was calculated to be 1.63.

(Figure 3 here)

### 3.2.3. Optimization of experimental parameters for FEN detection

#### 3.2.3.1. The effect of NiAl-DSS amount on the paste composition

The study of the effect of NiAl-DSS proportion within the CPE was expected to affect the electrode response. The cyclic voltammogram of FEN $5 \times 10^{-5}$ M in 0.1 M acetate buffer on CPE/NiAl-DSS prepared with various amounts of NiAl-DSS within the paste is shown in Figure 4A. The peak current intensity increases with the increasing amount of NiAl-DSS incorporated in the paste, up to a maximum value of 2% (Figure 4B), after which further increase in the amount of NiAl-DSS resulted in decrease in current peak intensity. The initial increase in peak current was due to the number of adsorption sites, which increase at the solution electrode interface, while the subsequent loss of peak current observed at NiAl-DSS proportions greater than 2% could be attributed to the fact that, NiAl-DSS is a poor conductive material. The high amount of this modifier within the carbon paste reduced the conductivity of the electrode. The optimum percentage of NiAl-DSS incorporated into the CPE was chosen to be 2% as the best compromise between the number of active sites and the conductivity of the paste.

(Figure 4 here)

#### 3.2.3.2. Effect of pH on FEN signal

The acidity of medium is a key parameter that can affect the mass transport on the electrode surface, especially when the redox process involves proton transfer as in the present case. Figure 5A represents the DPV curves of FEN $5 \times 10^{-5}$ M in acetate buffer 0.1 M on
CPE/NiAl-DSS when the pH was varied from 3 to 6. It was found that, the peak current and potential varied with the pH of the electrolytic solution. The results in Figure 5B showed that the sensitivity of the electrode increased in the pH range 4 < pH < 4.7 and then decreases with a further increasing solution pH. The optimum value is reached at pH 4.7. In fact, a low sensitivity obtained in the pH range 3 < pH < 4 can be attributed to the hydrolysis of the metal ions, and instability of LDH [47]. The loss of sensitivity observed for the pH value up to 4.7 could be explained by the fact that FEN was partially degraded in the pH range 5-6 [24]. Also shown in Figure 5A, the peak potential (Ep) shifted progressively to cathodic values with a variation of the pH from 3 to 6. The plot of peak potential as a function of pH of electrolytic solution is a straight line. The equation can be represented as

\[ E_p = -0.0376 + 1.0547 \times \text{pH} \quad (R^2 = 0.9942) \]

with a slope of -0.037 V/pH. This value is not close to the expected standard value -0.059 V/pH for an equal number of electrons and protons exchange during the electrode reaction as report in literature [23,24,48]. In fact, according to Nernst equation, the value of the slope (p) is given by Equation 3.

\[ p = \frac{m}{n} \times 0.059 \quad \text{(Equation 3)} \]

where \( m \) and \( n \) are number mole of proton and electron exchanged per mole of substance, respectively. The value of the slope obtained in this case indicates that, the number of electrons exchange is higher than that of protons. This can be probably due to the modification of the electrochemical mechanism of FEN compared to those proposed in literature [23,24,48]. In fact, according to Temgoua et al [43], oxidation of phenylurea compound as diuron took place with 2 electrons exchange in the present of one proton. In addition, Richard and Bengana [49] prove that in acidic medium (pH=4), FEN can be chemically degraded. Since no attempts has been made in this work to identify the oxidation products of FEN, furthers studies were need to elucidate a mechanistic pathway for the oxidation of FEN.
3.2.3.3. Repeatability and reproducibility of CPE/NiAl-DSS

The stability and reproducibility of the signal of FEN on CPE/NiAl-DSS was evaluated. Thus, a series of seven successive SWV experiments of the same electrode were performed in 50 μM of FEN solution (Figure SI 5), a coefficient of variation of 3% was noticed, indicating that the modified electrode has good reproducibility. The repeatability of CPE/NiAl-DSS was studied using 50 μM of FEN. The electrode was stored in a container for 5 days, the current response recorded decreases to 3.5% compared to the original peak current.

3.2.3.4. The effect of FEN concentration

The effect of concentration of analyte was studied under the optimized conditions established above. Figure 6B depicts a typical DPV peak recorded for a solution containing the pesticide obtained over the ranges of concentration of 0.5 to 1 μmol.L⁻¹ and 1 to 5 μmol.L⁻¹ in 0.1 M acetate buffer solution (pH 4.7). The plot of current versus FEN concentration shown the wide linearity (Figure 6A). With respect to the calibration graph, standard deviation (SD) of intercept and slope value of calibration curve, detection limit (3S/m) and quantification (10S/m) were found to be 1.8×10⁻⁹ mol.L⁻¹ and 6×10⁻⁹ mol.L⁻¹ respectively (in low concentration range). At low concentration, the sensitivity recorded was 3.50 μA/ μM a value 10 fold greater than that obtained in the high range concentration. A comparison of the performance of CPE/NiAl-DSS including the limit of detection and the linear range with those reported in the literature is shown in Table 1, which indicates that the proposed sensor exhibited detection limits lower than those reported by certain authors for trace analysis of some phenylurea pesticides [47,50,51,52].
3.2.3.5. Interferences and Analysis of real Samples

The performance of the sensor in the presence of some interfering compounds that can be found in environmental samples was investigated. Up to 1000-fold excess of Na\(^+\), K\(^+\), Ca\(^{2+}\), Cl\(^-\), SO\(_4^{2-}\) and Mg\(^{2+}\), no real influence of the FEN response was noticed. However, Pb\(^{2+}\) and Zn\(^{2+}\) at concentration 500 times excess over FEN significantly interfered with its. The formation of FEN-metal complex can explain these results. Glyphosate and Methylparathion at concentration 10 times excess over FEN hardly influence on the oxidation peak current of FEN, since the peak current changes below 7% and 15%, respectively. The presence of interference species like inorganic ions (Pb\(^{2+}\) and Zn\(^{2+}\)) and organic species (Glyphosate and Methylparathion) could somewhat reduce the selectivity of the method, and let us to propose their elimination from matrices before the quantification of FEN. In fact, according to literature, inorganic ion like Pb\(^{2+}\) can be remove in a medium using a typical chelating agent like ethylene diamine tetraacetic acid (EDTA) [57-59]. Glyphosate and methylparathion can be remove using smectite modified by organosilane [60,61].

The analytical applicability of the modified electrode was applied to the determination of FEN in real sample (A river water sample collected down-town Yaoundé-Cameroon). The filtered river water sample was characterized by a electrical conductivity of 150 \(\mu\)S/cm, a pH 5.5. A volume of 50 mL of the river water was first analyzed by using the optimized parameters established in this study and FEN was not detected. However if these samples were spiked with a standard solution of FEN and the corresponding responses were recorded. The quantitative recoveries of FEN in the real sample are summarized in Table 2. The
obtained values are in good agreement with the spiked value, indicating that the proposed method is a good alternative for the analytical determination of this pesticide in the sample.

(\textit{Table 2 here})

4. Conclusion

In this work, a NiAl-LDH intercalated by anionic surfactant was shown to be an effective material for the elaboration of an amperometric sensor for FEN. Before the use of this organo-LDH for sensing of FEN, infrared spectroscopy, X-ray diffraction and thermal, analysis results confirmed the intercalation of surfactant. Incorporating this organo-LDH into the carbon paste electrodes led to an increase in peak current, improving electrode sensitivity. An enhancement (2-fold) was obtained in the oxidation peak of FEN, when compared the response of the same electrode modified by pristine LDH. After optimization a detection limit of $1.8 \times 10^{-9}$ mol L$^{-1}$ was achieved. The proposed method was applied to quantify FEN in river water indicating that the proposed method is promising for the monitoring of FEN in various polluted media.

Acknowledgments

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