



Determination of linuron in water and vegetable samples using stripping voltammetry with a carbon paste electrode

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ABSTRACT

A carbon paste electrode was used for the electrochemical determination of linuron concentrations in water and vegetable extracts. Optimal conditions were established with respect to electrode activation (electrochemical pretreatment), time accumulation, potential accumulation, scan rate, and pH. The limit of detection achieved with a pre-concentration step was $23.0 \mu\text{g L}^{-1}$. Recovery measurements in vegetable extract and natural water samples were in the range of 98–103%, indicating that the proposed electrochemical method can be employed to analyze linuron in these matrices. The determination results were in good agreement with HPLC results.

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1. Introduction

Herbicides are the largest group of chemicals used as plant protection agents. One class of herbicides widely used pre- and post-emergence is substituted phenylureas—a less dangerous group of pesticides, given their low toxicity to mammals, high selectivity for specific pests, and good effectiveness at low dosages in common applications [1].

Phenylureas can enter the environment by different pathways, including spray drift, runoff from treated fields, and leaching into groundwater. Although photochemically unstable, phenylureas can persist in water for periods of days or weeks, depending on temperature and pH. Despite their typically low toxicity to mammals, some phenylureas have been reported as carcinogenic in experimental animals.

Phenylurea herbicides selectively control the germination of broadleaf weeds and grasses in all types of crops [2]. Because of their widespread usage, control of residues in ground and surface water is highly important. Phenylurea concentrations on the order of parts per million affect embryonic and neonatal development of fish and aquatic invertebrates [3].

Applied at high frequencies, they are useful as total weed killers, whereas many can be used at low rates for selective weed control in a wide range of crops. Linuron, or 3-[3,4-(dichlorophenyl)-

1-methoxy-1-methylurea] (Fig. 1), one of the most important commercial ureas, has good contact activity and the ability to kill emergent weed seedlings [4].

Although most multiresidue methods developed for determination of phenylureas in water, soil, and plant matrices based on chromatography [5], only a few electrochemical analytical studies of this pesticide have been reported. Most of them were based on voltammetric techniques, which have the advantage of usually obviating preliminary separation and purification for the analysis of complex biological materials. Voltammetric methods are therefore particularly useful in the analysis of turbid materials or samples that contain dispersed solid particles. They can be applied without sample pretreatment, a step commonly required in chromatographic analysis that increases both cost and analysis time [6,7].

Linuron determination based on single-sweep derivative polarography was first performed four decades ago, with an approximate limit of detection (LOD) of 2 g L^{-1} [5]. More recently, linuron has been determined voltammetrically in water and soil samples using a sepiolite-modified carbon paste electrode, with a LOD of $75 \mu\text{g L}^{-1}$ [3]. Also, stripping voltammetric methods using a carbon fiber microelectrode have been proposed for identification (qualitative analysis) of a mixture of carbendazim and linuron in soil samples (although only carbendazim determination has been optimized) [8] and for linuron determination in soil samples (with a LOD of $80 \mu\text{g L}^{-1}$) [9].

Some chromatographic methods for linuron determination involve electrochemical detection. The oxidation of two carba-

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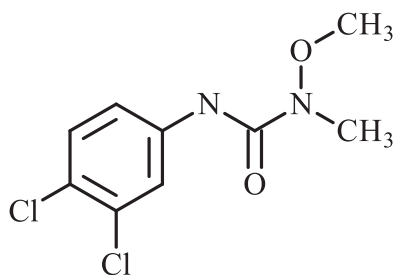


Fig. 1. Molecular structure of linuron.

mates, profam and chlorprofam, and nine ureas, including linuron, has been studied for analytical purposes using electrochemical detection with glassy carbon electrodes. Determination of these herbicides in model samples was performed in a continuous flow system using an amperometric wall-jet detector with and without high-performance liquid chromatographic (HPLC) separation. The LOD for linuron under optimized conditions was 0.24 mg L^{-1} [10]. The determination of a number of pesticides using HPLC, coupled with amperometric detection in model mixtures of benomyl, thiram, linuron, metoxuron, desmedipham, dicuron, lenacil, and fludioxonil dissolved in tap water and beetroot juice has also been performed. Using a glassy carbon electrode at 1.4 V with a thin-layer cell and a wall-jet cell, LODs of 0.17 mg L^{-1} and 0.20 mg L^{-1} , respectively, were measured for linuron [11].

Chromatographic methods for linuron determination using non-electrochemical detectors have also been proposed. For instance, HPLC was employed to determine linuron in potatoes, with estimated recovery values of 89.8% [12], whereas an analytical method based on HPLC with photodiode array detection permitted linuron determination in aqueous soil extracts containing different amounts of organic matter (0.7–11.7%), with a LOD of $10 \text{ } \mu\text{g L}^{-1}$ and recovery values from spiked samples in the range of 106.3–116.1% [13]. The latter method was employed to determine linuron adsorption in soils. In addition, a method based on solid-phase extraction (SPE) and liquid chromatography with UV mass spectrometric (MS) or diode array detection (DAD) has been developed for simultaneous determination of ten phenyl- and sulfonylurea herbicides in water, including linuron and one of linuron's most common degradation products. The linuron LODs using HPLC-DAD performed after SPE on UHQ water and river water samples were 18 and 34 ng L^{-1} , respectively [14]. For HPLC-MS performed after SPE on the same samples, the LODs were 15 and 17 ng L^{-1} , respectively. For these two methods, the relative standard deviations ($n=8$) for linuron determination at $0.1 \text{ } \mu\text{g L}^{-1}$ ranged from 13% to 22%.

Carbon paste electrodes (CPE) can be easily prepared and used to detect oxidation or reduction of electroactive compounds adsorbed on their surfaces [15]. Adsorptive stripping voltammetry is a very sensitive electroanalytical technique for the determination of surface active organic compounds and metal complexes in trace amounts [16]. Square-wave voltammetry (SWV), which allows for low LODs and very fast and effective scan rates, can successfully quantify the amount of analyte initially adsorbed [16,17].

In the present investigation, the electrochemical properties of linuron were studied using a new electrochemical method based on the electrochemical activation of a CPE. The proposed method was successfully applied to determine linuron in water and vegetable samples by stripping SWV.

2. Experimental

2.1. Equipments and reagents

All electrochemical measurements were performed with an Autolab PGSTAT12 (Ecochemie, Utrecht, The Netherlands). The

experiments were carried out in a three-electrode cell at room temperature ($25 \pm 1 \text{ } ^\circ\text{C}$), using a platinum wire as the counter-electrode, Ag/AgCl/KCl (3 mol L^{-1}) as the reference electrode, and a chemically unmodified CPE as the working electrode. The cell was placed in a Faraday cage in order to minimize background noise. The electrochemical techniques SWV and cyclic voltammetry (CV) were applied to investigate the electrochemical behavior of linuron.

A Micronal B-474 pH meter equipped with a combined glass electrode was used for adjusting pH values. Water purified in a Milli-Q system manufactured by Waters was used to prepare the solutions.

The pH values of the linuron solutions were adjusted using 0.2 mol L^{-1} Britton–Robinson (BR) buffer solutions ranging from pH 2 to pH 12. For use as supporting electrolytes, these buffer solutions were prepared by mixing solutions of H_3PO_4 , H_3BO_3 , and CH_3COOH and adjusting pH by adding suitable amounts of 2.0 mol L^{-1} NaOH. All others reagents were of analytical reagent grade.

Stock solutions of linuron (Sigma–Aldrich; 99.7% purity) were prepared by dissolving this herbicide in an acetonitrile:water (70:30, v:v) mixture.

The samples were analyzed using a Varian 210 analytical HPLC system equipped with a ternary solvent delivery module, an autosampler, and a photodiode array detector. Star WS software (Workstation) was used to measure the peak chromatogram areas. The HPLC column was an RP18 ($25 \text{ cm} \times 4.6 \text{ mm} \times 5 \text{ } \mu\text{m}$) reversed-phase column with a small pre-column ($2.5 \text{ cm} \times 3 \text{ mm}$) containing the same packing material used to protect the analytical column. Elution was carried out with a methanol:water:acetonitrile (40:40:20, v:v:v) isocratic solvent system for 20 min. The flow rate was 1.0 mL min^{-1} and $20 \text{ } \mu\text{L}$ was injected. All chromatographic analyses were performed at $22 \text{ } ^\circ\text{C}$.

2.2. Construction of the carbon paste electrode

Chemically unmodified carbon paste was prepared by mixing spectroscopic-grade graphite (Sigma–Aldrich; particle size $<20 \text{ } \mu\text{m}$) and mineral oil (Sigma–Aldrich) at 80%:20% (w:w). The mixture was homogenized in a mortar for 40 min and inserted into a 1.0 mL plastic syringe. Electrical contact was established via a copper wire.

2.3. Activation and renewal of the carbon paste electrode

The working electrode was placed in a measuring cell filled with 10 mL of BR buffer of known pH. Before each measurement, the buffer-immersed working electrode was activated by applying an anodic potential for 60 s. After electrochemical activation, a known amount of linuron solution was added to the cell containing the buffer solution. Before each voltammogram was recorded, the pesticide was accumulated on the CPE surface by applying an accumulation potential for 60 s under hydrodynamic conditions (magnetic stirring). CV potential scans were recorded starting in the negative direction, in the range from $+0.8 \text{ V}$ to -0.1 V vs. Ag/AgCl, KCl 3 mol L^{-1} . For SWV measurements, the potentials were also scanned in the negative direction from $+0.8 \text{ V}$ to -0.1 V . Activation and accumulation potentials ($+1.3 \text{ V}$ for CV, $+1.5 \text{ V}$ for SWV) were identical for both techniques. Before CPE activation, the electrode surface was renewed and smoothed on a paper sheet.

2.4. Preparation of samples

Known amounts of linuron were added to 10 mL water samples. The resulting solutions were filtered through a Millex filter ($0.45 \text{ } \mu\text{m}$ pore diameter) ($n=3$) and directly analyzed using HPLC.

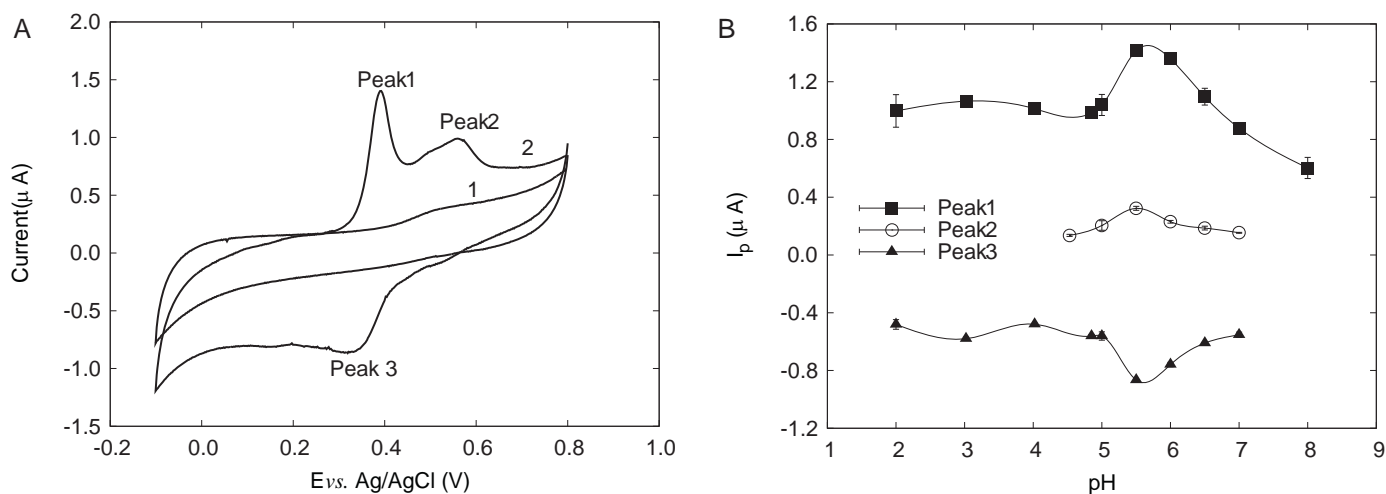


Fig. 2. (A) Cyclic voltammograms of 11 mg L^{-1} linuron in pH 5.5 BR buffer, recorded using a CPE, before (curve 1) and after (curve 2) electrochemical activation. (B) Variation of current peak vs. pH for voltammograms of 9.36 mg L^{-1} linuron, recorded using an electrochemically activated CPE. Experimental conditions: $E_{\text{acc}} = 1.3 \text{ V}$; $t_{\text{acc}} = 60 \text{ s}$; scan rate = 0.1 V s^{-1} .

Known concentrations of linuron dissolved in pH 5.5 BR buffer were directly added to other 10-mL water samples and analyzed using SWV.

Carrot, potato, and onion samples (5 g each) were triturated, macerated in 50 mL of water for 1 h, filtered through a Millex filter ($0.45 \mu\text{m}$ pore diameter), reconstituted with water in a 50 mL volumetric flask ($n = 3$), and directly analyzed using HPLC. Next, 1 mL aliquots from each of these extracts were transferred to a 10 mL volumetric flask. They were then completed with known concentrations of linuron and transferred to an electrochemical cell for measurements.

2.5. Quantification of linuron by HPLC and SWV

Linuron quantification using HPLC was performed by external calibration. The compound was separately dissolved in spectroscopic-grade methanol, yielding stock solutions that were diluted to five concentrations. A graphic plot of the means of areas against linuron concentrations was constructed. Linear least squares regression of peak areas as a function of weight was performed to determine the correlation coefficient. The equation parameters (slope and intercept) of the standard curve were used to obtain concentration values for all samples (water and vegetables).

Linuron quantification by SWV was based on the standard addition method under optimized conditions. Before measurements, 10 mL aliquots of BR buffer were placed into the electrochemical cell and an aliquot of extract was added. All measurements were made at room temperature.

3. Results and discussion

3.1. Electrochemical behavior

Linuron determination using SWV was performed with a pre-concentration step, which required previous study of the electrochemical behavior of linuron using CV, accomplished by applying an accumulation potential of 1.3 V for 60 s using CV, thus revealing two oxidations peaks (called peaks 1 and 2) and one reduction peak (called peak 3).

Fig. 2A shows cyclic voltammograms of linuron recorded after accumulation on the CPE surface under the experimental conditions described in Section 2.3—i.e., accumulation time (t_{acc}), 60 s; accumulation potential (E_{acc}), 1.3 V. Fig. 2(A) depicts the voltam-

mograms recorded for the electrolyte in the presence of linuron using a CPE before (curve 1) and after (curve 2) electrochemical pretreatment. The reverse scan in the first cycle reveals two anodic peaks ($E_{\text{p1}} = 0.39 \text{ V}$ and $E_{\text{p2}} = 0.56 \text{ V}$), while the starting scan reveals one cathodic peak ($E_{\text{p3}} = 0.33 \text{ V}$), as shown in voltammogram 2 in Fig. 2A. Peaks 1 and 3 were not detected in the first cycle in the potential range from -0.1 V to $+0.8 \text{ V}$ vs. Ag/AgCl, $\text{KCl } 3 \text{ mol L}^{-1}$, when the potential scan was recorded so as to start in the positive direction.

Electrochemical pretreatment (also termed electrochemical activation) of the working electrode surface is a simple procedure to enhance sensitivity and selectivity in voltammetric analyses of organic compounds [18]. Both anodic (or cathodic) polarization performed at extreme potentials and anodic-cathodic cycling are commonly employed procedures to pretreat the surface of carbon electrodes, including CPEs [15,16]. In the case of carbon pastes, the processes and phenomena associated with activation at a positive potential (anodization) are typically interpreted in terms of partial oxidation of the surface of graphite particles exposed to a solution. During activation, various oxygen-containing functional groups are formed and instantly protonated. As a result, these fragments become markedly hydrophilic, repelling the hydrophobic molecules of the binder. Anodization thus leads to removal of the lipophilic layer of the paste, causing the CPE surface to become hydrophilic and behave somewhat similarly to solid graphites [17,19].

3.2. Influence of pH on measurements

The effect of pH on the electrochemical behavior of linuron was examined using 0.2 mol L^{-1} BR buffer in the pH range from 2.0 to 8.0. For analysis, the pH values were adjusted by adding NaOH. Linuron concentration was 9.36 mg L^{-1} and the voltammograms were recorded from $+0.8$ to -0.1 V at a rate of 0.1 V s^{-1} after an accumulation time of 60 s at 1.3 V in all cases. Fig. 2B correlates current peaks and pH. For anodic peaks, maximum current was at pH 5.5. This was therefore the pH value selected for investigating the electrochemical behavior of linuron for analytical purposes.

The potential of anodic peak 1 was found to shift linearly towards more negative values with increasing pH values, indicating the intervention of protons in the electrochemical oxidation of linuron (Fig. 3). From pH 2.0 to 9.0, this linear dependence fits the

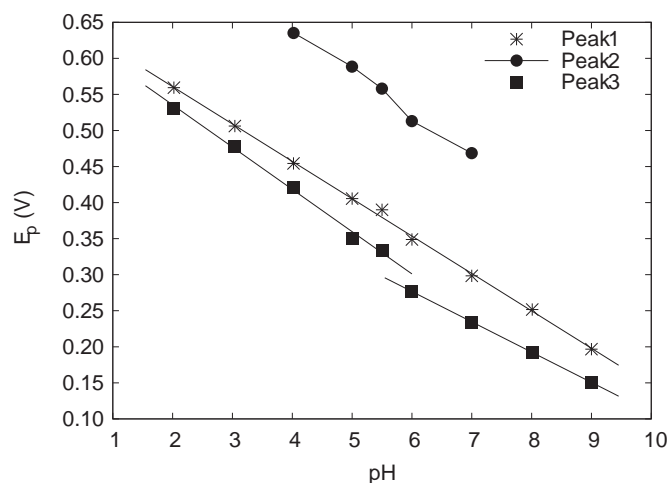


Fig. 3. Variation of potential peak vs. pH in 0.2 mol L⁻¹ BR buffer. Experimental conditions: scan rate, 0.1 V s⁻¹; $E_t = 1.3$ V; $t_t = 60$ s.

equation:

$$E_{p1} = 0.664 - 0.052 \text{ pH} \quad r = -0.999$$

For cathodic peak 3, the potential also shifted linearly towards more negative values with increasing pH, but it did so along two different slopes in the pH range considered. From pH 2.0 to 5.5, the potential shift obeys the equation:

$$E_{p3} = 0.653 - 0.058 \text{ pH} \quad r = -0.998$$

The slope obtained in this case (practically the Nernst equation theoretical value) means that the same numbers of protons and electrons are involved in the electrochemical process [20].

From pH 6.0 to 9.0, the linear variation of the cathodic peak potential fits the equation:

$$E_{p3} = 0.529 - 0.042 \text{ pH} \quad r = -0.998$$

Application of an accumulation potential of 1.3 V to CV promotes linuron electrochemical oxidation through loss of methoxy and methyl groups. This initially involves elimination of the methoxy group (replaced by a hydrogen atom) through formation of 3-(3,4-dichlorophenyl)-1-methylurea and formic acid. Subsequently, the intermediate hydroxymethyl derivative undergoes another oxidative process of *N*-demethylation through formation of 3-(3,4-dichlorophenyl)-urea and formaldehyde. In early studies, both steps were detected as the appearance of two coupled peaks at a sepiolite-modified CPE [3] and a carbon fiber microelectrode [9]. In the present investigation, however, a single cathodic peak was detected at an electrochemically activated CPE. The cathodic peak detected at a more positive potential (compared with 0.45 V at pH 2 for the sepiolite-modified CPE [3]) is probably obscured by a broad-banded peak 3. Actually, a cathodic wave appears at +0.55 V at pH 5.5, whereas a pronounced peak 3 is seen at 0.33 V (Fig. 2A, curve 2).

3.3. Square-wave frequency (f)

For linuron determination using SWV, the CPE was subjected to anodic electrochemical pretreatment by polarization at a potential of 1.5 V for 75 s to ensure improved peak current response. Pretreatment was repeated before each measurement.

Two different linear correlations between peak current and frequency were confirmed for peak 1 (the main peak in the SWV voltammograms shown in Fig. 4). For peak 1, peak current correlated linearly with f , but not with $f^{1/2}$. These patterns had

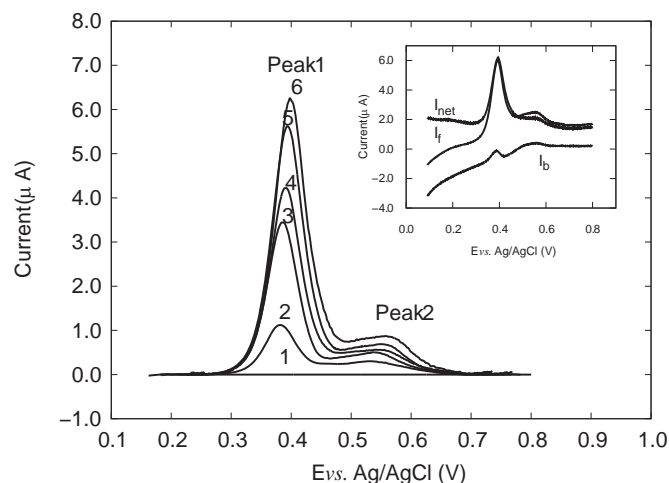


Fig. 4. SWV for 11 mg L⁻¹ linuron in 0.2 mol L⁻¹ BR buffer at pH 5.5; (1) BR buffer pH 5.5; (2) 30 s⁻¹; (3) 50 s⁻¹; (4) 80 s⁻¹; (5) 120 s⁻¹; (6) 160 s⁻¹. Insert: net response (I_{net}) and its forward (I_f) and backward (I_b) components. Experimental conditions: $E_t = 1.5$ V; $t_t = 60$ s; $\Delta E = 1.05$ mV; $a = 9$ mV.

previously been attributed by Lovrić and Komorsky-Lovrić [21] to irreversible oxidation without adsorption of reagent or reagent and product (peak current vs. $f^{1/2}$) and irreversible reaction with adsorption of reagent (peak current vs. f) [22]. In a quasi-reversible process, the relationship between current peak and frequency is not linear. If a redox reaction is totally irreversible, regardless of product adsorption, the relationship between peak current and frequency is linear [21]. This allows peak 1 to be assigned to irreversible oxidation with reagent adsorption and allows the electroanalytical methodology proposed for linuron determination to be considered an adsorptive stripping square-wave voltammetric method.

The potential of the square-wave peak, E_p , correlates linearly with the standard potential $E_{A/B}^0$, the logarithms of the adsorption constant K , the standard reaction rate constant k_r , the square-wave frequency f , and the square-wave amplitude a :

$$E_p = E_{A/B}^0 + \frac{RT(\ln K)}{nF} + \frac{RT(\ln kr - \ln 2f)}{\alpha nF} - 0.35a \quad (1)$$

Eq. (1) predicts E_p with an accuracy of ± 5 mV and exactly predicts the slope $\partial E_p / \partial \ln f = -RT / \alpha nF$ only when the reagent is adsorbed [22]. The SW half-peak width $\Delta E_{p1/2}$ depends only on the number of electrons and the transfer coefficient:

$$E_{p1/2} = (63.5 \pm 5) \text{ mV} / \alpha n \quad (2)$$

Since half-peak width is independent of SW frequency, the αn parameter can be determined from Eq. (2). Considering the value of $E_{p1/2}$ for linuron (57.7 mV), use of Eq. (2) yields $\alpha n = 1.10$ if $\alpha = 0.5$ (irreversible process) and $n = 2$ (two electrons involved in the oxidation of linuron) for peak 1.

Dependence of the current peak on the square-wave frequency is linear in the range from 50 to 120 s⁻¹ and the slope $\partial i_p / \partial f$ is 2.86×10^{-8} A s (k_r). The system has irreversible characteristics, as it obeys the relation $\log k_r / 2f \leq -5$ [22,23]. The absence of reduction peaks along the backward component (I_b , insert to Fig. 4) confirms the irreversibility of peak 1.

3.4. Pulse amplitude (a)

Amplitude of the pulse applied to the electrode, a , is another factor influencing measurement sensitivity. As a is increased, a linear increase in the peak current is observed up to 60 mV. Linear correlation is observed between i and a in the range from 10 to

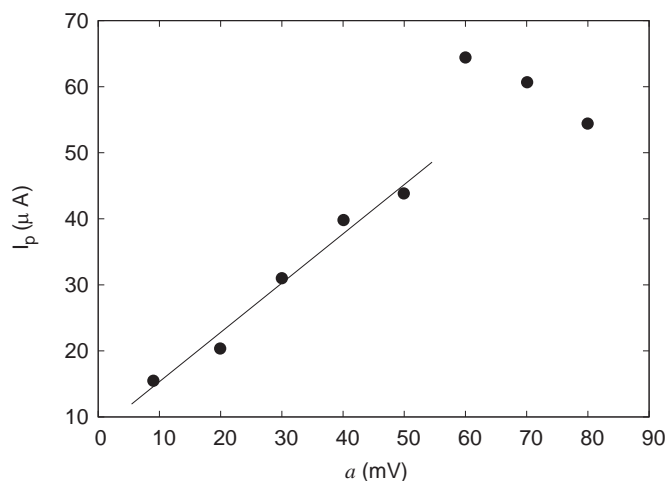


Fig. 5. Dependence of peak current on pulse amplitude for 11 mg L^{-1} linuron in 0.2 mol L^{-1} BR buffer at pH 5.5. Experimental conditions: $E_t = 1.5 \text{ V}$; $t_t = 60 \text{ s}$; $f = 120 \text{ s}^{-1}$; $\Delta E = 1.05 \text{ mV}$.

50 mV (Fig. 5). For this reason, 60 mV was the value selected for conducting analytical determinations.

3.5. Influence of accumulation time (t_{acc})

Accumulation time (t_{acc}) was investigated in the range from 0 to 90 s. At pH 5.5, I_p was highest at 60 s, decreasing thereafter (Fig. 6).

3.6. Influence of accumulation potential (E_{acc})

The accumulation potential (E_{acc}) varied significantly in the range from 0.5 to 1.7 V, with maximum peak current at $E_{acc} = 1.4 \text{ V}$ (Fig. 7). $E_{acc} = 1.4 \text{ V}$ was therefore the value selected for further experiments. A higher peak current is obtained by applying this E_{acc} , as compared with an open circuit.

3.7. Influence of herbicide concentration

The LOD was calculated in accordance with the IUPAC definition [24,25] (i.e., the smallest quantity or concentration of analyte in a solution that can be detected with reasonable certainty for a given analytical procedure). This limit is expressed in concentration units and is the ratio between the standard deviations of blank responses

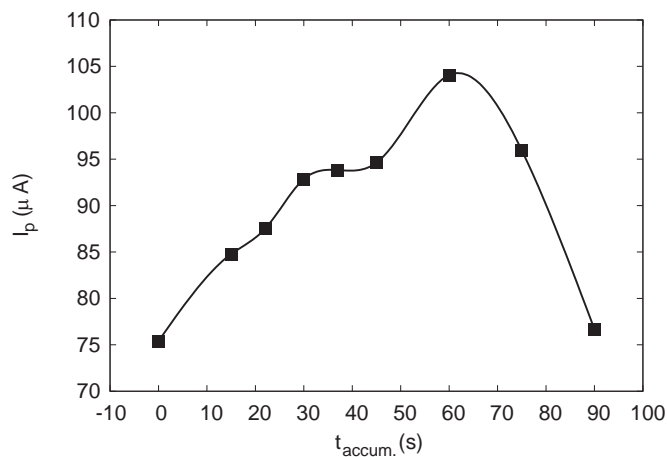


Fig. 6. Influence of accumulation time for 11 mg L^{-1} linuron in 0.2 mol L^{-1} BR buffer at pH 5.5. Experimental conditions: $E_t = 1.5 \text{ V}$; $t_t = 60 \text{ s}$; $f = 120 \text{ s}^{-1}$; $\Delta E = 7.95 \text{ mV}$; $a = 60 \text{ mV}$.

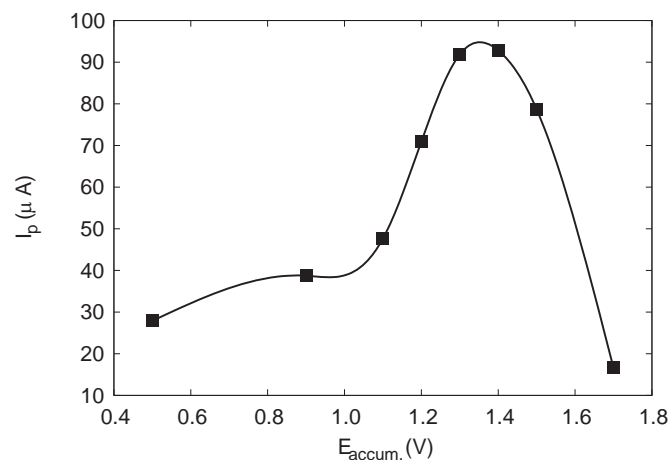


Fig. 7. Influence of accumulation potential for 11 mg L^{-1} linuron in 0.2 mol L^{-1} BR buffer at pH 5.5. Experimental conditions: $E_t = 1.5 \text{ V}$; $t_t = 60 \text{ s}$; $f = 120 \text{ s}^{-1}$; $\Delta E = 7.95 \text{ mV}$; $a = 60 \text{ mV}$; $t_{acc} = 60 \text{ s}$.

Table 1

Analytical parameters obtained from calibration curves for linuron at a carbon paste electrode using the proposed square-wave voltammetric method.

Parameters	Values
Correlation coefficient	0.997
Intercept (A)	9.81×10^{-8}
Slope ($A/\mu\text{g L}^{-1}$)	0.01627
Limit of detection ($\mu\text{g L}^{-1}$)	23.00
Relative standard deviation	1.248×10^{-7}

Table 2

Analytical parameters obtained from calibration curves for linuron, using HPLC.

Parameters	Values
Correlation coefficient	0.999
Intercept (A)	7.76×10^{-9}
Slope ($A/\mu\text{g L}^{-1}$)	0.001432
Relative standard deviation	2.007×10^{-10}

and the slope of the analytical curve Eq. (3).

$$\text{LOD} = \frac{3\text{SB}}{s} \quad (3)$$

LOD was therefore obtained by applying Eq. (3), considering the analytical curve of linuron in the concentration range from 25.75 to $309.02 \mu\text{g L}^{-1}$. Table 1 lists the analytical parameters obtained from the calibration curves using SWV.

The limit of detection by HPLC was determined by injecting linuron solutions ($n = 10$; $20 \mu\text{L}$ each) and then decreasing the concentrations of the samples until a peak having a signal-to-noise ratio of 3 was detected. The corresponding concentration was considered to be the minimum detectable concentration. The limit of quantification was similarly determined—i.e., it corresponded to the chromatographic peak having a signal-to-noise ratio of 10. LOD and LOQ by HPLC were 2.01 and $6.63 \mu\text{g L}^{-1}$, respectively.

The parameters (slope and intercept) of the standard curve were used to obtain the concentration values for all samples (Table 2).

4. Application to samples

4.1. Linuron recovery from natural and distilled water using voltammetry and HPLC

Recovery experiments were performed by spiking distilled and natural water samples with known amounts of linuron in the concentration range to be investigated, yielding values of around

Table 3

Linuron recovery from water samples at a carbon paste electrode using square-wave voltammetry and HPLC.

Linuron	SWV		HPLC	
	Natural	Distilled	Natural	Distilled
Added ($\mu\text{g L}^{-1}$)	59.66	59.20	59.66	59.20
Found ($\mu\text{g L}^{-1}$)	57.36	58.07	59.13	59.03
Recovered (%)	96.00	98.00	99.11	99.71
RSD (%)	3.70	2.90	1.01	1.00

RSD: relative standard deviation (mean of three measurements).

Table 4

Linuron recovery from vegetable extract samples at a carbon paste electrode, using HPLC.

Linuron	Extract (SWV)			Extract (HPLC)		
	Carrot	Potato	Onion	Carrot	Potato	Onion
Added ($\mu\text{g L}^{-1}$)	50.25	59.80	58.36	50.25	59.80	58.36
Found ($\mu\text{g L}^{-1}$)	49.78	61.35	57.36	50.03	60.07	57.90
Recovered (%)	99.06	103.00	98.00	99.56	100.45	99.21
RSD (%)	3.78	4.67	2.23	1.03	0.98	0.90

RSD: relative standard deviation (mean of three measurements).

96–98%, which demonstrates the viability of the proposed electroanalytical methodology. The principal results are presented in Table 3.

Linuron recovery from water samples using the proposed voltammetric method showed optimum agreement with the values achieved with HPLC. The presence of adsorbent organic materials capable of interacting with linuron explains the low recovery values from natural water samples, for both techniques.

4.2. Linuron recovery from vegetable extracts

Known concentrations of linuron were added to potato, carrot, and onion extracts and readings were taken from three samples. The recovery values are described in Table 4. LOD and LOQ were 2.01 and $6.63 \mu\text{g L}^{-1}$ using HPLC, respectively.

Linuron recovery from vegetable extract samples using the proposed stripping voltammetric method exhibited good agreement with the values achieved with HPLC, with discrepancies of around 2%.

5. Conclusions

The proposed electroanalytical method using an electrochemical activated CPE ensured sensitive and accurate determination

of linuron in water (distilled and natural) and vegetable (carrot, potato, and onion) matrices. In addition, the proposed electroanalytical method based on adsorptive stripping SWV has the advantage of being simpler, faster, and less costly than HPLC, which makes it a good alternative for the analysis of linuron in vegetable and water samples.

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