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Full Paper

Square-Wave Voltammetric Determination of Nanomolar Levels of Linuron in Environmental Water Samples Using a Glassy Carbon Electrode Modified with Platinum Nanoparticles within a Dihexadecyl Phosphate Film

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A new sensitive method for linuron determination using a glassy carbon electrode modified with platinum nanoparticles within a dihexadecyl phosphate film (PtNPs-DHP/GCE) and square-wave voltammetry was proposed. The PtNPs-DHP/GCE was characterised by scanning electron microscopy and the diameter of the Pt nanoparticles was between 13 and 34 nm. The electrochemical behaviour of linuron was studied using cyclic voltammetry and an irreversible anodic peak was obtained at a potential of 1.2 V in 0.1 mol L^{-1} phosphate buffer (pH 3.0) solution. The analytical curve, obtained by square-wave voltammetry after accumulation, was linear in the linuron concentration range from 1.0 to 74.0 nmol L^{-1}, with a detection limit of 0.61 nmol L^{-1}. This sensitive analytical method was successfully applied for linuron determination in environmental water samples with results that showed good agreement with those obtained using a comparative HPLC method.

Introduction

Herbicides are the largest group of chemicals used as plant protection agents, and of these, phenylurea is used on pre- and post-emergent crops. Phenylurea can persist in water for a few days or weeks depending on conditions such as temperature and/or pH[1] while degradation via microbial activity is very slow and accumulation to toxic levels can occur. Biological contamination by phenylurea was studied in adults rats, where the presence of phenylurea caused the development of tumours.[2]

Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea] is one of the most important commercial phenylureas that is widely used for the selective control of broadleaf weeds and grasses in fruit or field crops, cereals, and shelter belts.[3] A wide range of analytical methods have been applied to the analysis of linuron that are mostly based on chromatographic techniques.[4–7] Nevertheless, several methods are prone to drawbacks such as high cost, complicated and lengthy procedures, and unsuitability for practical use.

Electrochemical techniques, such as voltammetry, are a promising alternative to classical approaches due to their relatively low operating cost, good miniaturisation potential, and

rapid and sensitive detection procedures suitable for faster analyses. Some methods for detecting linuron by voltammetric techniques have been previously reported. Hernandez et al.[8] used differential pulse voltammetry and a carbon-paste electrode modified with 20 % w/w sepiolite. Gonzalez de la Huebra et al.[9] determined linuron in soil extracts using a carbon fibre microelectrode. More recently, Đorđević et al. developed procedures used to detect linuron in spiked river water samples and a commercial formulation using a tricresyl phosphate-based carbon paste electrode,[3] a home-made non-modified glassy carbon electrode, and a modified boron-doped glassy carbon electrode.[10] de Lima et al. employed a carbon paste electrode for electrochemical determination of linuron concentrations in water and vegetable extracts.[11]

The modification of electrode surfaces with metal and metal oxide nanoparticles has been used extensively in the development of sensors as nano-sized transition metal particles have unique properties that differ from those of the bulk metal. The addition of nanoparticles to the surface of conductive substrates is expected to have advantages over conventional electrodes by providing large surface areas, high mass transport, enhanced

signal-to-noise ratios, as well as excellent catalytic and electro-catalytic activities. However, the catalytic properties of these metal particles strongly depend on the size, shape, and catalyst support.[12–16] In the literature, the electrocatalytic performance of platinum nanoparticles (PtNPs) has been used for the sensing of biological molecules, oxidation of methanol, formic acid, and the reduction of oxygen.[17–22]

It is worth mentioning that the immobilisation of nanoparticles on substrates such as graphite, carbon nanotubes, glassy carbon, and other metals for sensing purposes has been studied extensively in recent years.[23] Our research group had studied and applied different kinds of surfactants and polyelectrolytes for nanomaterial immobilisation.[24–27] Dihexadecyl phosphate (DHP) is a hydrophobic surfactant that has two long hydrocarbon chains linked to a phosphate group, which self-assembles into multiple bilayer structures similar to lipid bilayers and exhibit characteristic of gel-to-liquid crystal phase transition.[25]

The aim of this study was the preparation, characterisation, and testing of a new sensor based on a glassy carbon electrode modified with PtNPs within a dihexadecyl phosphate film (PtNPs-DHP/GCE) in order to investigate the electrochemical behaviour of linuron as well as its detection in environmental water samples and commercial samples.

Experimental

Reagents and Solutions

All reagents were of analytical grade and the solutions were prepared with water purified with a Milli-Q system (Millipore®) (resistivity $>18\,M\Omega$ cm). The reagents used were potassium chloride (Merck), hydrochloric acid (Merck), sulfuric acid (Sigma–Aldrich), potassium hexacyanoferrate(III) (Synth), dihexadecyl phosphate (Aldrich), sodium phosphate dibasic (Synth), monobasic sodium phosphate (Synth), boric acid (Merck), phosphoric acid (Mallinckrodt), linuron (Aldrich), and ethanol (Mallinckrodt). Acetic acid, sodium acetate, platinum(IV) chloride and sodium citrate were obtained from Sigma–Aldrich. H_3PO_4 (85 %) and NaH_2PO_4 that were used to prepare the supporting electrolyte were purchased from Merck. All other chemicals were of analytical grade.

A $0.1\,mol\,L^{-1}$ phosphate buffer solution (pH 3.0) was used as the supporting electrolyte for linuron determination and a $0.1\,mol\,L^{-1}$ linuron stock solution was prepared daily in this solution. Standard linuron solutions were prepared from the stock solution in $0.1\,mol\,L^{-1}$ phosphate buffer solution (pH 3.0) and bubbled with ultrapure N_2 gas to prevent chemical oxidation.

Apparatus

Voltammetric measurements were carried out using an Autolab Ecochemie PGSTAT-20 (Utrecht, Netherlands) potentiostat/galvanostat controlled with the *GPES 4.9* software. All the electrochemical experiments were conducted at 25.0 ± 0.5°C in a three-electrode single-compartment glass cell using a glassy carbon electrode (diameter $= 3$ mm) modified with PtNPs within a dihexadecyl phosphate film (PtNPs-DHP/GCE) as the working electrode, Pt foil as an auxiliary electrode, and an Ag/AgCl (saturated KCl) reference electrode.

The pH was determined using a Denver Instrument pH meter (UB10 Ultra Basic) employing a combined glass electrode with an Ag/AgCl (saturated KCl) external reference electrode.

The comparative method employed for linuron determination was HPLC using a LC-10AT Shimadzu system with an UV–visible detector set at 250 nm (SPD-M10AVP) and a Shim-Pack CLC-ODS (4.6 nm i.d. × 150 mm length, 5 μm particle size) chromatographic column. The mobile phase consisted of methanol/water/acetonitrile (40 : 40 : 20, v/v/v) at a flow rate of $1.0\,mL\,min^{-1}$ with an injection volume of 20 μL.[11]

Field-emission gun scanning electron microscopy (FEG-SEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were conducted on a Supra 35-VP equipment (Carl Zeiss, Germany) with an electron beam energy of 25 keV. A disk cut from a glassy carbon electrode (GCE) was used for immobilising the dispersion of PtNPs-DHP using the same casting method employed for the electrochemical analysis electrode.

PtNPs Synthesis

The PtNPs were synthesised by the Turkevich method,[28] through the citrate-mediated reduction of platinum chloride ($PtCl_4$). The PtNPs dispersion was obtained by adding 4.0 mL of $0.5\,mmol\,L^{-1}$ platinum chloride to 200 mL of water at 85°C with stirring then adding 2.0 mL of $0.3\,mol\,L^{-1}$ sodium citrate solution with stirring for 7 min. The solution was placed in an ice-bath to cool to room temperature and was stored in an amber flask at room temperature.

Preparation of PtNPs-DHP Film

The GCE was mechanically polished with sandpaper (P4000), rinsed with water and acetone then air-dried. The PtNPs-DHP film was prepared by dispersing 1.0 mg DHP in 1.0 mL of PtNPs by ultrasonication for 15 min, then adding 10 μL to the GCE surface using the casting method, and then allowed to dry for 24 h. The study of the amount of deposited platinum was carried out previously and 10 μL was the best one.[16,26]

Analytical Procedure

Linuron determination was performed using square-wave voltammetry (SWV). The SWV parameters used and the optimal chemical conditions (supporting electrolyte and pH) were also evaluated. After optimising the parameters, SW voltammograms for linuron were obtained within the potential range from 0.0 to +1.5 V versus Ag/AgCl (saturated KCl) with an accumulation time of 270 s at open circuit potential, a frequency of 50 Hz, pulse amplitude of 40 mV, and potential increment of 7.5 mV. All measurements were carried out in triplicate ($n = 3$) for each concentration.

Environmental water samples (A1 and A2) were collected: A1 was collected from the Ribeirão Piraí river (GPS Latitude – 23°26′201″S and Longitude – 47°05′790″W) and A2 was collected from the Jundiaí river (GPS Latitude – 23°2′055″S and Longitude – 47°29′176″W). A 20 μL aliquot of the $1.0 \times 10^{-6}\,mol\,L^{-1}$ linuron standard solution was added for every 2 mL of sample. The commercial sample A3 (linuron concentration of $450\,g\,L^{-1}$) was purchased from a local market and properly diluted.

Results and Discussion

Characterisation of PtNPs-DHP Film

First, the particle size, morphology, and elemental compositions of the PtNPs-DHP film (dried over the GCE surface) were characterised by SEM. As shown in Fig. 1, two types of particle structures were observed on the surface, the cubic particles could be from the salt solution used to produce the nanoparticles and the small particles (grey) were the PtNPs. EDX analysis was

performed to identify the elements present on the electrode surface and results showed a high percentage of carbon (94.11 %), oxygen (4.55 %), platinum (0.29 %), chlorine (1.02 %), and phosphorus (0.02 %); those values were in agreement with the expectations considering the chemicals used in the film preparation. It is important to note the carbon detected by EDX was associated with the glassy carbon used as a substrate.

The proposed electrode was characterised by cyclic voltammetry. Fig. 2a shows the voltammetric behaviour of a polycrystalline bulk platinum electrode (dashed line) and PtNPs-DHP/GCE (solid line). The voltammetric profile was well defined for platinum: hydrogen region (-0.2 V to $+0.2$ V versus Ag/AgCl (saturated KCl)), electric double layer ($+0.2$V to 0.7 V versus Ag/AgCl (saturated KCl)), and platinum oxidation region (0.7 V versus Ag/AgCl (saturated KCl)). The same behaviour was observed for the PtNPs supported on the GCE (solid line).
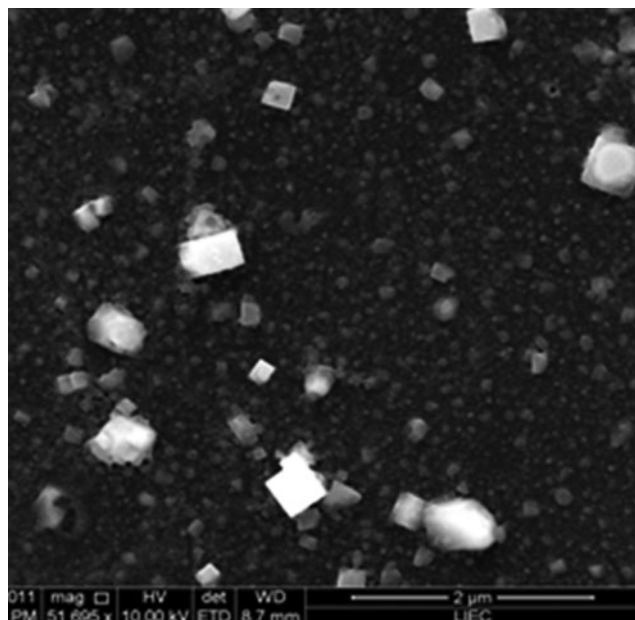

Fig. 1. FEG-SEM micrograph of PtNPs-DHP film onto a glassy carbon surface.

The electroactive areas of the GCE, DHP/GCE, and PtNPs-DHP/GCE electrodes were estimated through the redox response of the $[Fe(CN)_6]^{4-}$ species (1.0×10^{-3} mol L^{-1} in 0.1 mol L^{-1} KCl) according to the Randles–Ševćik equation (Eqn 1):[29]

$$I_{pa} = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \qquad (1)$$

where I_{pa} is the anodic peak current (A), A is the electroactive area (cm^2), D is the diffusion coefficient of the $[Fe(CN)_6]^{4-}$ species in solution (6.2×10^{-6} cm^2 s^{-1}), n is the number of electrons transferred in the redox reaction, v is the potential scan rate (V s^{-1}), and C is the concentration (mol cm^{-3}) of $[Fe(CN)_6]^{4-}$.

The electroactive areas of the GCE, DHP/GCE, and PtNPs-DHP/GCE electrodes were estimated at 0.028, 0.005, and 0.020 cm^2, respectively. The DHP/GCE showed a lower electroactive area compared with GCE because there was a blockage of active sites and difficulty in the electron transfer and/or diffusion of electroactive species at the electrode surface, thereby decreasing the current signal. However, when the GCE was modified with PtNPs-DHP, the electroactive area increased by a factor of four with respect to the DHP/GCE. The advantage of using DHP dispersions is due to the greater adherence and stability of the film provided by this surfactant.[25,27] Fig. 2b shows the voltammetric behaviour of PtNPs-DHP/GCE for 1.0×10^{-3} mol L^{-1} $[Fe(CN)_6]^{4-}$ in 0.1 mol L^{-1} KCl solution.

Electrochemical Behaviour of Linuron Herbicide Using a PtNPs-DHP/GCE

The cyclic voltammetric behaviour of PtNPs-DHP/GCE (solid line) towards linuron was compared with those of bare GCE (dotted line), a Pt electrode (dash dotted line), and a DHP/GCE (dashed line) (Fig. 3). The proposed sensor showed a well-defined analytical signal for the analyte of approximately $+1.2$ V. Of note was the small anodic current (Fig. 3 inset) used with the GCE and DHP/GCE electrodes. This indicated that the incorporation of PtNPs into the DHP film could provide an increased current signal for linuron determination.

Studies were performed to determine the pH, supporting electrolyte, and adsorption time needed to optimise the analytical signal. Fig. 4a, b shows the effect of pH on the anodic peak
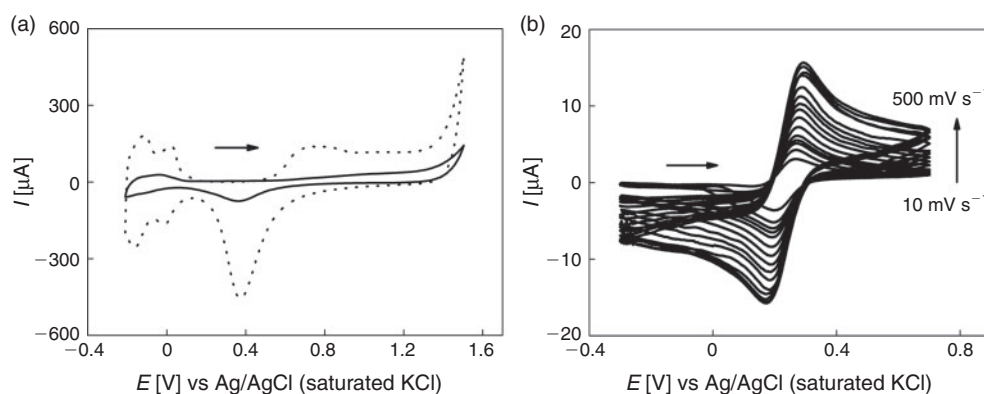

Fig. 2. (a) Cyclic voltammograms of bare Pt (dotted line) and PtNPs-DHP/GCE (solid line) in 0.1 mol L^{-1} H$_2$SO$_4$ solution; $v = 50$ mV s^{-1}. (b) Cyclic voltammograms of PtNPs-DHP/GCE for a 1.0×10^{-3} mol L^{-1} $[Fe(CN)_6]^{4-}$ in 0.1 mol L^{-1} KCl solution at different scan rates (10–500 mV s^{-1}).

current and anodic peak potential, respectively. The highest anodic peak current was obtained at pH 3.0 (Fig. 4a). The peak potential shifted linearly (with $R^2 = 0.971$) with increasing pHs and a slope of 0.052 was obtained – a value near the Nernst eqauation ($0.0592 \times E$/pH) – indicating that an equal number of protons and electrons were involved in the oxidation mechanism. The proposed oxidation mechanism for linuron (Fig. 4c) is based on dimerisation, involving two electrons and two protons, where the dimer is bonded to nitrogen I close to the aromatic
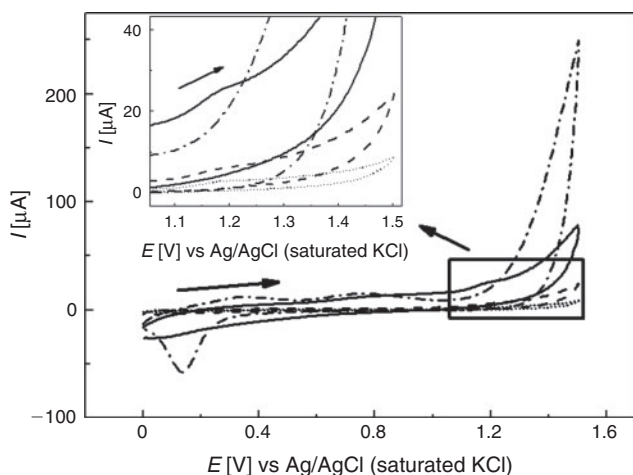
ring. This mechanism is similar to that for another pesticide (diuron);[30,31] both pesticides showed a small difference in structure (methoxy group on nitrogen II) and the oxidation potentials are comparable i.e. ∼0.85 V for diuron and 1.2 V for linuron.

Three different supporting electrolytes were evaluated at pH 3.0 (0.5 mol L^{-1} phosphate buffer, Britton–Robinson buffer, and acetic acid). The phosphate buffer presented a well-defined baseline as well as a better definition for the oxidation peak and was selected for further experiments. It is known that platinum-based electrodes may have adsorptive characteristics.[32,33] Hence, linuron adsorption onto the sensor surface was examined. The results confirmed adsorption and after the stripping, no anodic current was observed, thus an accumulation time range from 30 to 300 s was studied and the selected value was 270 s.

Optimisation of SWV Parameters and Analytical Curve for Linuron Using PtNPs-DHP/CGE

The instrumental parameters for SWV were studied with the aim of obtaining a well-defined peak and high anodic peak current for linuron. The experimental parameters and their corresponding investigated ranges were as follows: frequency, $10\,Hz \leq f \leq 200\,Hz$); pulse amplitude, $10\,mV \leq a \leq 150\,mV$); and potential increment, $1.0\,mV \leq \Delta E_s \leq 10\,mV$). The best results for the SWV parameters were as follows: $f = 50\,Hz$; $a = 40\,mV$; and $\Delta E_s = 7.5\,mV$.

The SW voltammograms obtained after successive additions of the respective standard solution of linuron using the PtNPs-DHP/CGE electrode are shown in Fig. 5. The plot of the anodic current versus linuron concentration was found to
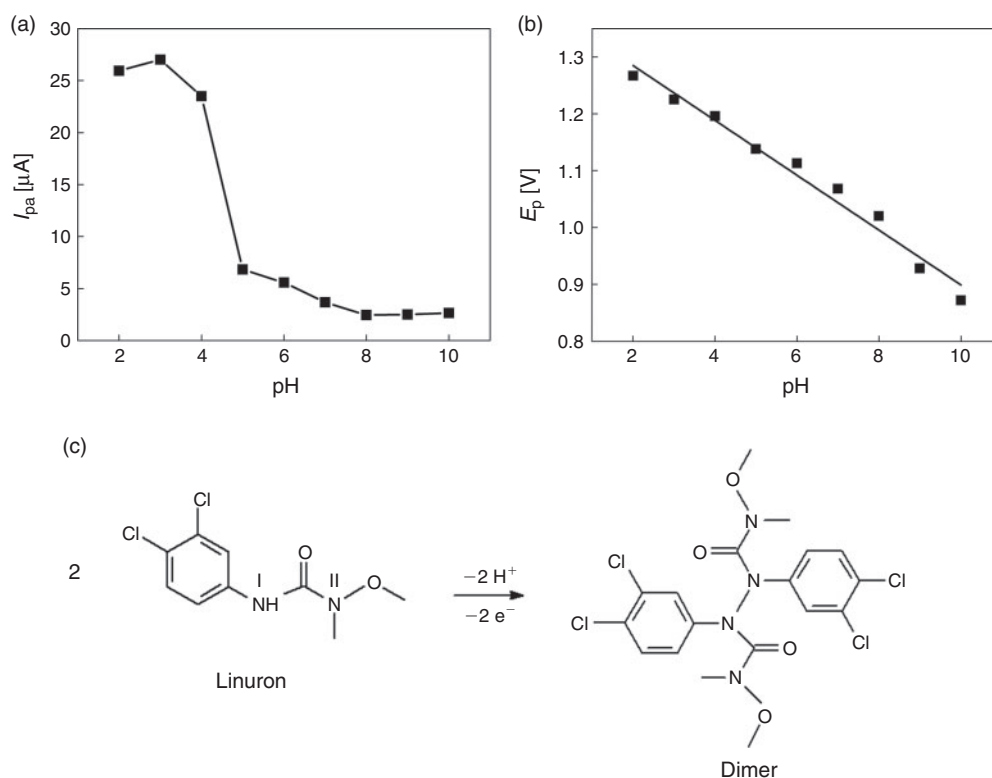

Fig. 3. Cyclic voltammograms using different electrodes: Pt (dash dotted line), GCE (dotted line), DHP/GCE (dashed line), PtNPs-DHP/GCE (solid line) in the presence of 1.0×10^{-4} mol L^{-1} linuron in 0.1 mol L^{-1} phosphate buffer (pH 3.0); $v = 50$ mV s^{-1}. Inset shows a close up of the oxidation peak.

Fig. 4. (a) Anodic peak current as function of pH. (b) Potential as a function of pH using PtNPs-DHP/GCE in the presence of 1.0×10^{-4} mol L^{-1} linuron in 0.1 mol L^{-1} phosphate buffer (pH 3.0); $v = 50$ mV s^{-1}. (c) Schematic representation of the mechanism for linuron oxidation on PtNPs-DHP/GCE.
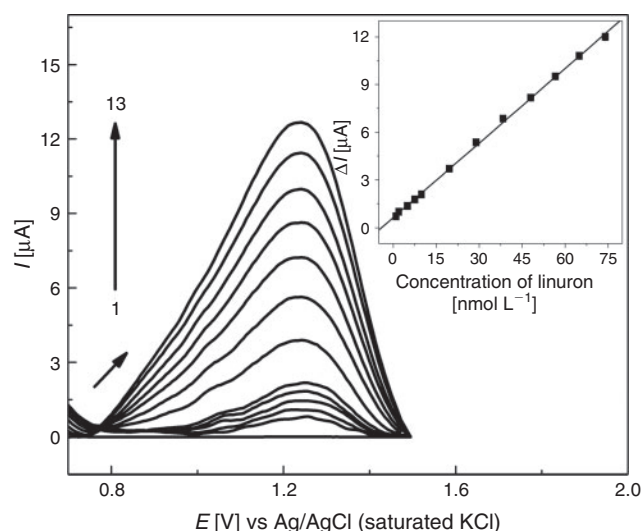
Fig. 5. SW voltammograms for: (1) blank, (2) 1.0, (3) 2.0, (4) 5.0, (5) 7.0, (6) 9.9, (7) 20.0, (8) 29.0, (9) 38.0, (10) 48.0, (11) 56.0, (12) 65.0, and (13) 74.0 nmol L^{-1} linuron using PtNPs-DHP/GCE under the optimum parameters in 0.1 mol L^{-1} phosphate buffer. Inset shows analytical curve for linuron.

Table 1. Effect of several species on the determination of 10 nmol L^{-1} linuron (standard) in environmental water samples

Interferents	Concentration	Interference [%]
Alkaline ions/alkaline earth	100 nmol L^{-1}	0.8
Metallic ions	100 nmol L^{-1}	−5.2
Humic acid	0.1 % w v^{-1}	0.2
Vermicompost	0.1 % w v^{-1}	7.4

Table 2. Results obtained in the determination of linuron (mg L^{-1}) in environmental water samples and commercial samples comparing HPLC (standard method) and SWV (proposed) methods

Samples	HPLC	SWV	Relative error[A] [%]
A	2.49 ± 0.01	2.42 ± 0.02	−2.81
B	2.54 ± 0.06	2.69 ± 0.02	5.90
C	2.73 ± 0.04	2.34 ± 0.03	−14.29

[A]100 × (SWV value − HPLC method)/HPLC method.

be linear over the concentration range of 1.0–74 nmol L^{-1} with the corresponding best fit equation: I_{pa} (μA) = 6.39 × 10^{-7} + 156.23[linuron] (mol L^{-1}), with a correlation coefficient of 0.999. The detection limit of 0.6 nmol L^{-1} was calculated as 3 times the standard deviation of the blank ($n = 10$) divided by the slope of the analytical curve.

The repeatability of a single PtNPs-DHP/GCE sensor was assessed by successive determinations ($n = 10$) using a 29 nmol L^{-1} linuron solution under the optimised parameters previously described. The relative standard deviation (RSD) obtained was 1.78 % for 10 successive measurements without renewing the electrode surface, indicating very good sensor stability. The repeatability of the method was investigated for the 74 nmol L^{-1} linuron solution using five independently prepared electrodes. The RSD of the measurements for the five different electrodes was 1.64 %, indicating good repeatability for the proposed method.

Interferents and Comparative Method

The effect of possible interferents, such as alkaline earth and alkaline ions (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}), metallic ions (Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}), humic acid and vermicompost, were investigated by separate addition to 10 nmol L^{-1} linuron solution (pH 3.0). The results (Table 1) showed that for all species tested, a change of less than 10 % in the electrode response was observed, indicating that these species did not significantly interfere with linuron determination experiments using the proposed method.

The performance of the proposed analytical method was evaluated for environmental water samples (samples A and B) collected from Ribeirão Piraí and Jundiaí Rivers as well as a commercial sample (sample C) as described in the Experimental section. The HPLC (experimental conditions are provided in the Experimental section) results were used for comparison with results obtained using the proposed voltammetric method. The results presented in Table 2 employing the proposed method and the comparative HPLC method were in good agreement at a confidence level of 95 % (F test and paired t-test ($t_{calculated}$ = 0.658 exp ($t_{tabulated}$) = 4.303).

Table 3 presents comparison of the proposed method with other electroanalytical methods for linuron determination. The proposed voltammetric method had a lower detection limit and a wider linear range at low concentrations than other methods reported in the literature. Furthermore, the proposed method presented a detection limit that is below the maximum levels of linuron permitted in wastewater according to the Brazilian

Table 3. Comparison of analytical parameters obtained for linuron determination using the proposed method (PtNPs-DHP/GCE) and other methods (various electrodes)

CP, carbon paste; CM, carbon microfibres; Sepiolite (magnesium silicate), Mg$_4$Si$_6$O$_{15}$(OH)$_2$·6H$_2$O; GC, glassy carbon; BDGC, boron-doped glassy carbon

Electrode	Detection limit (nmol L^{-1})	Concentration range (nmol L^{-1})	Reference
CP	92	103–1240	de Lima et al.[11]
CM	320	361–5260	Gonzalez de la Huebra et al.[9]
CP/Sepiolite	300	–	Hernandez et al.[8]
CP/Tricresyl phosphate	1500	5050–177 000	Đorđević et al.[3]
GC	1000	28000–130 000	Đorđević et al.[10]
BDGC	600	5000–100 000	Đorđević et al.[10]
PtNPs-DHP/GCE	0.6	1–74	This work

environmental protection agency (CONAMA)[34] (i.e. $2.00 \times 10^{-7} \, mol \, L^{-1}$ and Canadian Water Quality Guidelines[35] (i.e. $2.81 \times 10^{-8} \, mol \, L^{-1}$).

Conclusions

A modified glassy carbon electrode (GCE), Pt nanoparticles, and dihexadecyl hydrogen phosphate film electrode (PtNPs-DHP/GCE) were assembled using a simple drop coating procedure and used for the electroanalytical determination of linuron at extremely low concentrations by SWV. The proposed method had a lower detection limit $(0.6 \, nmol \, L^{-1})$ and a wider linear range $(1.0-74.0 \, nmol \, L^{-1})$ than other methods. The proposed method was used for linuron determination in environmental water samples and the results obtained were in agreement with HPLC (confidence level of 95 %). The results of this study indicated that the combination of SWV and PtNPs-DHP/GCE is a simple, rapid, and inexpensive alternative analytical method for linuron determination.

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