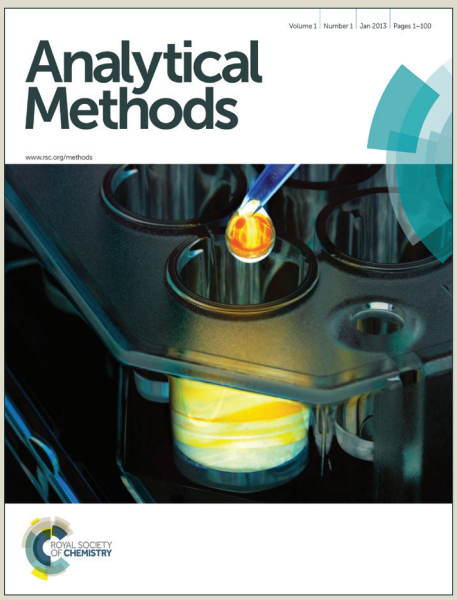
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Electroanalytical determination of the linuron herbicide using a cathodically pretreated boron-doped diamond electrode: comparison with a boron-doped diamond electrode modified with platinum nanoparticles

Luiz C. S. Figueiredo-Filho[a]*, Elen R. Sartori[a,b], and O. Fatibello-Filho[a]

[a]Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13560-970, São Carlos – SP, Brazil

[b]Departamento de Química, Universidade Estadual de Londrina, C.P. 10.011, 86057-970, Londrina – PR, Brazil

* Corresponding author.

Tel.: +55 16 33518055

E-mail: figueiredo.lcs@gmail.com (L.C.S. Figueiredo-Filho)

Abstract

The determination of linuron using differential-pulse voltammetry (DPV) and a cathodically pretreated boron-doped diamond electrode is proposed. Cyclic voltammetry results showed one irreversible oxidation peak for linuron at 1.29 V (*vs.* Ag/AgCl (3.0 mol L^{-1} KCl)) in 0.04 mol L^{-1} Britton-Robinson (BR) buffer solution (pH 2.0). Under optimized DPV conditions, a linear analytical curve was obtained for the linuron concentration range 0.61–26.0 μmol L^{-1} with a detection limit of 0.18 μmol L^{-1}. Similar responses (linearity and sensitivity) were obtained employing a boron-doped diamond electrode modified with platinum nanoparticles. The proposed method was successfully applied in the determination of the linuron in natural water samples with recoveries ranging from 90.9% to 104%.

Keywords: Linuron determination, herbicides, Boron-doped diamond electrode, Cathodic pretreatment, Platinum nanoparticles.

Introduction

At present, there are numerous studies in the literature involving the evaluation of electrochemical sensors for the determination of pesticides, including carbon paste [1-4], carbon nanotubes [5, 6], mercury [7-9], bismuth film [10-12], and different types of nanomaterials [13-16]. However, there are few studies using a boron-doped diamond electrode (BDDE) for the determination of this kind of analyte [17]. One of the main characteristics of this electrode is low surface adsorption by organic compounds [18]. This quality is very important in pesticide determination since the biggest problem is poisoning of the electrode surface after a few measurements. Other important characteristics of BDDE is a large useful potential range, resistance to corrosion in highly aggressive media, stable and low background current, and good stability in long-term response [18, 19].

Since nanoparticles have been intensively studied, many properties have been observed, such as optical and catalytic properties. Electrochemical/electroanalytical researchers have begun to use this type of nanomaterial more frequently in recent years [20-22]. In the most cases, an improvement in terms of electroanalytical behavior can be observed, showing higher catalytic performance, mass transport, *etc.*, when nanoparticle-modified electrodes were compared with macroelectrodes; these improvements are chiefly attributable to size effects. Several methods have been used for preparing metal clusters [23-30]. Most of these methods can produce nanoparticles on a supported surface or on colloidal dispersions, which are subsequently used to modify the surface of the electrodes.

Pesticides, when used properly, can save up to 40% of crop losses – however, when pesticides are misused, the consequences of environmental and public health can

be very serious. Urea/phenylurea herbicides are among the most widely used in the culture of trees [31], and their action is very similar to the triazine pesticides, *i.e.*, inhibition of photosynthesis by interruption of the Hill reaction [11, 31]. The toxicity effects of these herbicides on fish and invertebrates have been studied, and it was observed that concentrations in the order of parts per million (ppm) affected the embryonic development [32].

One of the most commercialized urea pesticides is linuron, or 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (Figure 1), which efficiently eliminates emergent weed seedling by contact [33]. The linuron half-life in soil is 40–70 days, and the soil water can retain milligrams per day, which can persist for several weeks [34], depending on the water temperature and pH.

Insert Figure 1 here

The first electroanalysis of linuron was performed by Grover [35] using a polarography technique. In recent years, linuron was determined by different electrodes, such as carbon-fiber microelectrodes [31], modified carbon-paste electrodes [1, 4], glassy carbon, and boron-doped glassy carbon [3]. Meng and Ma [36] reported HPLC analysis of linuron, which involved amperometric detection using a glassy carbon electrode. All of these electrodes were used for different samples, such as natural water, soil, and vegetables.

The purpose of this work was to investigate the electrochemical behavior of linuron in aqueous solution at a BDDE and a BDDE modified with Pt nanoparticles

(PtNP-BDDE) by cyclic, square wave, and differential pulse voltammetries to propose a sensitive method to determine detect linuron in natural water samples.

Experimental

Reagents and standards

All solutions were prepared with Millipore Milli-Q nanopure water (resistivity > 18 MΩ cm). All chemicals used were of analytical grade, and were used directly without any further purification. H_2SO_4 was obtained from Merck, while platinum(IV) chloride and linuron were from Sigma.

A stock solution of 1.2 mmol L^{-1} linuron was prepared before use in ethanol. Linuron working solutions were prepared by dilution of the stock solution with Britton-Robinson (BR) buffer solution (pH 2.0). This buffer was prepared by mixing 0.04 mol L^{-1} of acetic, orthophosphoric, and boric acids, and adjusting the pH by adding suitable amounts of 2.0 mol L^{-1} sodium hydroxide. All linuron solutions were protected from light by using amber glass material.

Apparatus

The voltammetric measurements were carried out using an Autolab PGSTAT-30 (Ecochemie) potentiostat/galvanostat controlled with GPES 4.0 software. Electrochemical experiments were conducted in a three-electrode single-compartment glass cell (with degassing facilities for bubbling N_2), including a BDDE (8000 ppm; 0.26 cm^2 exposed area; Adamant, Switzerland) as the working electrode, a Pt foil as the

auxiliary electrode, and an Ag/AgCl (3.0 mol L^{-1} KCl) reference electrode. Cyclic, differential-pulse, and square-wave voltammetric measurements were carried out in a 10.0-mL electrochemical cell. All experiments were carried out at room temperature (25ºC ± 1°C).

Prior to the experiments, the BDDE was electrochemically pretreated in a 0.5 mol L^{-1} H_2SO_4 solution, either anodically by applying 0.5 A cm^{-2} for 20 s, or cathodically by applying –0.5 A cm^{-2} for 80 s. After the anodic or cathodic pretreatment, the BDDE surface is predominantly oxygen- or hydrogen terminated, respectively.

For BDDE modification, the platinum nanoparticles (PtNPs) were electrochemically deposited as described by Hutton et al. [37], who used a fixed potential of –940 mV *vs.* Ag/AgCl (3.0 mol L^{-1} KCl) for 5 s in a solution containing 1.0 mmol L^{-1} $PtCl_4$ in 0.1 mol L^{-1} HCl solution.

The pH was measured at 25.0ºC ± 0.5°C using an Orion pH-meter, Expandable Ion Analyser, model EA-940, employing a combined glass electrode with an Ag/AgCl (3.0 mol L^{-1} KCl) external reference electrode.

Measurement procedures

After optimizing the experimental parameters for the proposed methods, the analytical curves were constructed by adding small volumes of concentrated standard solutions of linuron. The limit of detection (LOD) was calculated as three times the standard deviation for the blank solution divided by the slope of the analytical curve.

The samples of natural water (A1 and A2) were collected from the Tietê River in Salto City, Brazil. For each sample, an aliquot was transferred to three different calibration flasks. After this, the samples were carefully spiked with a linuron standard solution to obtain concentrations of 1.1, 3.2, and 5.6 μmol L^{-1}.

Results and Discussion

Voltammetric behavior of linuron in a BDDE

Initially, the effect of the pretreatment of the BDDE was investigated. The electrode was anodically (0.5 A cm^{-2} for 20 s) or cathodically (–0.5 A cm^{-2} for 80 s) pretreated in 0.5 mol L^{-1} H_2SO_4 solution and its response was assessed for 24.0 μmol L^{-1} linuron solution at a BDDE in a BR buffer solution (pH 2.0), as presented in Figure 2. As can be seen, better peak definition and a higher current magnitude were obtained employing cathodically pretreated BDDE, as was observed previously for other compounds (*e.g.,* chlorophenols [38], acetylsalicylic acid [39], sildenafil citrate [40], β-blockers [41], and paracetamol and caffeine [42]). Moreover, from this voltammogram, it can be seen that no reduction peaks were observed, indicating an irreversible anodic process.

Next, the cathodic pretreatment time on the analytical response was investigated. The magnitude of current increased with the cathodic pretreatment up to 80 s, then remained constant. Consequently, all subsequent experiments were carried out using a cathodically pretreated BDDE by applying –0.5 A cm^{-2} for 80 s, which was performed daily before starting the voltammetric measurements. This cathodic pretreatment was preceded by an anodic pretreatment (0.5 A cm^{-2} for 20 s) in order to guarantee the oxidation of possible contaminants.

Insert Figure 2 here

Effect of pH and composition of the supporting electrolyte

The influence of pH (between 2.0 to 6.0) on the peak current for 24.0 μmol L^{-1} linuron by employing phosphate buffer solution is shown in Figure 3A and 3B. A decrease in pH led to a current magnitude increase, and the potential shifted to more positive values. The peak current presented a maximum value for phosphate buffer solution at pH 2.0.

Insert Figure 3 here

Next, the influence of the different supporting electrolytes with identical pH values (pH 2.0), including 0.1 mol L^{-1} phosphate buffer, 0.1 mol L^{-1} BR buffer, sulfuric acid, nitric acid, hydrochloric acid, and 0.1 mol L^{-1} sodium nitrate (pH adjusted with 2.0 mol L^{-1} nitric acid) solutions on the electrochemical oxidation of 24.0 μmol L^{-1} linuron at the BDDE were investigated. The best results (higher current magnitude and less positive potential) were obtained with the BR buffer solution. Thus, this solution was chosen as the supporting electrolyte for further experiments.

Effect of scan rate

The effect of the potential scan rates from 5 to 500 mV s^{-1} on the voltammetric response of BDDE was investigated for 24.0 μmol L^{-1} linuron in BR buffer solution at pH 2.0 (Figure 4). The cyclic voltammograms revealed that the peak currents increased and the peak potential shifted as the scan rate increased. The anodic peak current varied linearly with the square root of the scan rate (inserted in Figure 4), suggesting that the linuron oxidation follows a diffusion-controlled mechanism [43] according to the linear relationship: I_{pa} (A) = 1.43 × 10^{-6} + 3.01 × 10^{-5} $v^{1/2}$ (r = 0.991).

Insert Figure 4 here

Optimization of Square wave voltammetric (SWV) and Differential pulse voltammetric (DPV) parameters and analytical curves using a BDDE

For the development of the electroanalytical procedures for the determination of linuron in natural water samples, the effect of experimental parameters that affect the SWV and DPV techniques was investigated using 6.2 μmol L^{-1} linuron in BR buffer solution (pH 2.0) employing a cathodically pretreated BDDE.

For SWV, the corresponding investigated ranges were: 10–75 s^{-1}, for square wave frequency *f*; 10–150 mV, for pulse amplitude *a*; 1–5 mV, for the scan increment ΔE_S. The obtained optimized values were f = 75 s^{-1}, a = 40 mV, and ΔE_S = 4 mV. The SWV technique was used to determine the number of electrons transferred in the redox process using eq. (1) [44]:

$$\Delta E_{ap}/\Delta \log f^{1/2} = 2.3RT/\alpha nF \quad \text{eq. (1)}$$

where α is the transfer coefficient, T is the temperature, F Faraday constant, R universal gas constant and n the number of electrons transferred. The n value was calculated to be 3, indicating that the oxidation of linuron involves three electrons per molecule (Figure 5).

Insert Figure 5 here

For DPV, the ranges studied were 10–150 mV for pulse amplitude (a), 2–20 mV s^{-1} for scan rate (ν), and 3–20ms for modulation time (t). The optimized values were a = 100 mV, ν = 15 mV s^{-1}, and t = 3 ms.

After optimizing the experimental parameters for the proposed methods, the analytical curves were constructed by adding small volumes of concentrated standard solutions of linuron. The respective analytical curves for linuron by DPV (Figure 6) and SWV (Figure ESI1) techniques using a cathodically pretreated BDDE were I_{ap}/μA = –0.33 + 0.67 [linuron/(μmol L^{-1})] (r = 0.9991) and I_{ap}/μA = –0.089 + 0.31 [linuron/(μmol L^{-1})] (r = 0.9998). The linear ranges were 0.61–26.0 μmol L^{-1} and 0.46–26.0 μmol L^{-1}, respectively. The calculated LOD values were 0.18 μmol L^{-1} and 0.12 μmol L^{-1}, respectively. As can be observed, the best values for analytical parameters, such as linearity and sensitivity, were obtained for the DPV technique. The DP voltammograms and the respective analytical curve obtained for the linuron reference solutions at different concentrations (0.61–26.0 μmol L^{-1}) in a BR buffer solution (pH 2.0) using a cathodically pretreated BDDE is shown in Figure 6.

Insert Figure 6 here

The intra-day repeatability of the peak current was determined by successive measurements (n = 10) of 1.2 μmol L^{-1} linuron solution, and a relative standard deviation of 0.56% was obtained. The inter-day repeatability of the peak current was evaluated by measuring the peak current for similar fresh solutions over a period of 5 days, and a relative standard deviation of 2.1% was obtained.

Physical characterization of Pt nanoparticles on the BDDE surface

Initially, particle size and morphology of the PtNPs-BDDE and BDDE (Figure 7A and 7B) was characterized by scanning electron microscopy (SEM). Two types of particle structures were observed (Figure 7B); the cubic particle is the BDD and the small particles (white) are the PtNPs. Moreover, the PtNP distribution was analyzed, and the histogram (ESI1) showed an average of 13.4 nm and 84.6% of the PtNPs had a size between 7.5 and 22.5 nm.

Insert Figure 7 here

Modification of the BDDE surface with Pt nanoparticles

The results obtained employing a cathodically pretreated BDDE were compared with those obtained using a PtNP-BDDE. Figure 8 shows the cyclic voltammograms for a 30 μmol L^{-1} linuron standard solution using a BDDE (solid line) and a PtNP-BDDE (dashed line). An increase in the resistivity of the surface-modified electrode was observed, and a decrease in the magnitude of the current (analytical signal), when the BDDE was surface-modified with PtNPs. This can be attributed to a passivation of the BDDE surface with the addition of PtNPs, since the cathodic pretreatment causes a hydrogen termination over the BDDE surface, and it is known that platinum has high affinity for such terminations. This leads to a blockage of the electroactive area of the BDDE. Although the PtNP-BDDE presented a lower analytical response than BDDE to linuron determination, in order to evaluate the possibility of using the PtNP-BDDE as a sensor to determine linuron, the experimental parameters of SWV and DPV techniques were evaluated in BR buffer solution (pH 2.0), and the construction of analytical curves (Figure ESI2 and ESI3) was carried out.

For SWV, the corresponding investigated ranges were: 10–75 s^{-1}, for square wave frequency f; 10–75 mV, for pulse amplitude a; 1–7 mV, for the scan increment ΔE_S. The obtained optimized values were f = 50 s^{-1}, a = 50 mV, and ΔE_S = 4 mV. For DPV, the ranges studied were 10–150 mV for pulse amplitude (a), 2–20 mV s^{-1} for scan rate (ν), and 3–25ms for modulation time (t). The optimized values were a = 100 mV, ν =7.5 mV s^{-1}, and t = 10 ms.

Insert Figure 8 here

The analytical parameters thus obtained for both electrodes (cathodically pretreated BDDE and PtNP-BDDE) using DPV and SWV are summarized in Table 1. As can be seen, the results (linear range and sensitivity) obtained employing a cathodically pretreated BDDE are similar to those obtained using a PtNP-BDDE. Thus, a cathodically pretreated BDDE using DPV was selected for the determination of the linuron in natural water samples.

Insert Table 1 here

Comparison of the analytical parameters obtained using other electrodes for linuron determination

The voltammetric determination of the pesticide linuron is based on its oxidation at the working electrode with an accumulation step [2, 4, 31, 45], or its direct determination employing carbon-based electrodes [3, 46]. Table 1 presents the comparison between the analytical performance of the BDDE and previous voltammetric procedures for the determination of linuron. The use of a BDDE for direct determination of linuron led to an improvement in the detection limit when compared with the results obtained using a carbon-paste electrode containing tricresyl phosphate (TCP-CPE) [3], a glassy carbon electrode (GCE) and a modified boron-doped glassy carbon electrode (GCBE) [46]. Moreover, in this work, it was not necessary to use an organic reagent of high toxicity for dissolution of linuron (*e.g.,* methanol and acetonitrile) and no modification or renewing mechanical of the surface of electrode, as reported by other authors [2-4, 31, 45, 46].

Insert Table 2 here

Application of the proposed method in the determination of linuron in natural water samples

The cathodically pretreated BDDE was applied for the determination of linuron in previously spiked natural water samples (see Experimental section).

Addition and recovery experiments were performed by adding different amounts of standard solutions of linuron to each sample, followed by analysis using the proposed DPV method. Sets of triplicate enrichments were added with increasing concentration of the linuron, yielding values of around 90.9–104% (Table 3), indicating that there were no matrix interferences for these samples analyzed by the proposed voltammetric method.

Insert Table 3 here

Conclusions

The present study shows that linuron can be determined in natural water samples by differential-pulse voltammetry using a cathodically pretreated BDDE. A BDDE without modification showed better analytical characteristics than a PtNP-BDDE because a passivation of the surface of the BDDE occurs with the addition of nanoparticles to the modified electrode. Optimization of the experimental parameters yielded a detection limit for linuron of 0.18 μmol L^{-1}, and a relative standard deviation

of less than 0.6% for 1.2 μmol L^{-1} linuron solutions (n = 10). Addition-recovery tests were satisfactory, yielding values of around 90.9–104%, and a relative error of less than 5.5%. In addition, the reported results demonstrate that the combination of DPV and a cathodically pretreated BDDE is a feasible alternative for the analytical determination of linuron in water samples without the necessity of using organic reagents for dissolution of this herbicide or modification of the surface of the electrode for the linuron determination.

Acknowledgements

The authors gratefully acknowledge financial support and scholarships from the Brazilian funding agencies FAPESP (Proc. 2014/04284-6, 2010/20754-1, and 2009/14454-8) CAPES (PDSE-1505122) and CNPq.

References

1. Z. Papp, I. Svancara, V. Guzsvany, K. Vytras and F. Gaal, *Microchim. Acta*, 2009, **166**, 169-175.
2. F. de Lima, F. Cozzi, A. R. Fiorucci, C. A. L. Cardoso, G. J. Arruda and V. S. Ferreira, *Talanta*, 2011, **83**, 1763-1768.
3. J. Dordevic, Z. Papp, V. Guzsvany, I. Svancara, T. Trtic-Petrovic, M. Purenovic and K. Vytras, *Sensors*, 2012, **12**, 148-161.
4. P. Hernandez, J. Vicente, M. Gonzalez and L. Hernandez, *Talanta*, 1990, **37**, 789-794.
5. M. P. Siswana, K. I. Ozoemena, D. A. Geraldo and T. Nyokong, *J. Solid State Electrochem.*, 2010, **14**, 1351-1358.
6. S. S. Fan, F. Xiao, L. Q. Liu, F. Q. Zhao and B. Z. Zeng, *Sens. Actuator B-Chem.*, 2008, **132**, 34-39.
7. V. Mirceski, D. Guziejewski, S. Skrzypek and W. Ciesielski, *Croat. Chem. Acta*, 2010, **83**, 121-126.
8. C. G. Tsiafoulis and C. G. Nanos, *Electrochim. Acta*, 2010, **56**, 566-574.
9. T. Sarigul and R. Inam, *Electrochim. Acta*, 2009, **54**, 5376-5380.
10. L. C. S. Figueiredo-Filho, V. B. dos Santos, B. C. Janegitz, T. B. Guerreiro, O. Fatibello-Filho, R. C. Faria and L. H. Marcolino, *Electroanalysis*, 2010, **22**, 1260-1266.
11. L. C. S. Figueiredo-Filho, D. C. Azzi, B. C. Janegitz and O. Fatibello-Filho, *Electroanalysis*, 2012, **24**, 303-308.
12. D. Du, X. P. Ye, J. D. Zhang and D. L. Liu, *Electrochim. Acta*, 2008, **53**, 4478-4484.
13. B. C. Janegitz, L. C. S. Figueiredo-Filho, L. H. Marcolino, S. P. N. Souza, E. R. Pereira and O. Fatibello-Filho, *J. Electroanal. Chem.*, 2011, **660**, 209-216.
14. V. A. Pedrosa, R. Epur, J. Benton, R. A. Overfelt and A. L. Simonian, *Sens. Actuator B-Chem.*, 2009, **140**, 92-97.
15. H. Parham and N. Rahbar, *J. Hazard. Mater.*, 2010, **177**, 1077-1084.
16. S. Marin and A. Merkoci, *Electroanalysis*, 2012, **24**, 459-469.
17. L. C. Melo, D. De Souza, P. de Lima-Neto and A. N. Correia, *Electroanalysis*, 2010, **22**, 2502-2510.
18. M. Hupert, A. Muck, R. Wang, J. Stotter, Z. Cvackova, S. Haymond, Y. Show and G. M. Swain, *Diam. Relat. Mat.*, 2003, **12**, 1940-1949.
19. Y. V. Pleskov, *Russ. J. Electrochem.*, 2002, **38**, 1275-1291.
20. J. Chomoucka, J. Drbohlavova, M. Masarik, M. Ryvolova, D. Huska, J. Prasek, A. Horna, L. Trnkova, I. Provaznik, V. Adam, J. Hubalek and R. Kizek, *Int. J. Nanotechnol.*, 2012, **9**, 746-783.
21. L. Rassaei, M. Amiri, C. M. Cirtiu, M. Sillanpaa and F. Marken, *Trac-Trends Anal. Chem.*, 2011, **30**, 1704-1715.
22. L. Xiang, C. J. Zhao and J. H. Wang, *Sens. Lett.*, 2011, **9**, 1184-1189.
23. J. C. Claussen, A. Kumar, D. B. Jaroch, M. H. Khawaja, A. B. Hibbard, D. M. Porterfield and T. S. Fisher, *Adv. Funct. Mater.*, 2012, **22**, 3399-3405.
24. D. D. La, C. K. Kim, T. S. Jun, Y. Jung, G. H. Seong, J. Choo and Y. S. Kim, *Sens. Actuator B-Chem.*, 2011, **155**, 191-198.
25. T. F. Hsieh, C. C. Chuang, Y. C. Chou and C. M. Shu, *Mater. Des.*, 2010, **31**, 1684-1687.

26. S. E. W. Jones and R. G. Compton, *Curr. Anal. Chem.*, 2008, **4**, 177-182.
27. Z. Y. Wu, L. G. Chen, G. L. Shen and R. Q. Yu, *Sens. Actuator B-Chem.*, 2006, **119**, 295-301.
28. S. H. Liu, M. T. Wu, Y. H. Lai, C. C. Chiang, N. Y. Yu and S. B. Liu, *J. Mater. Chem.*, 2011, **21**, 12489-12496.
29. J. Hu, X. Lu and J. S. Foord, *Electrochem. Commun.*, 2010, **12**, 676-679.
30. X. G. Li and I. M. Hsing, *Electrochim. Acta*, 2006, **51**, 5250-5258.
31. M. J. G. de la Huebra, P. Hernandez, Y. Ballesteros and L. Hernandez, *Talanta*, 2001, **54**, 1077-1085.
32. P. Y. Caux, R. A. Kent, G. T. Fan and C. Grande, *Environ. Toxicol. Water Quality*, 1998, **13**, 1-41.
33. H. Katsumata, H. Asai, S. Kaneco, T. Suzuki and K. Ohta, *Microchem J.*, 2007, **85**, 285-289.
34. M. Biziuk, A. Przyjazny, J. Czerwinski and M. Wiergowski, *J. Chromatogr. A*, 1996, **754**, 103-123.
35. R. Grover and R. J. Hance, *Soil Sci.*, 1970, **109**, 136-&.
36. Z. Y. Meng and Y. J. Ma, *Microchem J.*, 1996, **53**, 371-375.
37. L. Hutton, M. E. Newton, P. R. Unwin and J. V. Macpherson, *Anal. Chem.*, 2009, **81**, 1023-1032.
38. H. B. Suffredini, V. A. Pedrosa, L. Codognoto, S. A. S. Machado, R. C. Rocha and L. A. Avaca, *Electrochim. Acta*, 2004, **49**, 4021-4026.
39. E. R. Sartori, R. A. Medeiros, R. C. Rocha and O. Fatibello-Filho, *J. Braz. Chem. Soc.*, 2009, **20**, 360-366.
40. E. F. Batista, E. R. Sartori, R. A. Medeiros, R. C. Rocha and O. Fatibello-Filho, *Anal. Lett.*, 2010, **43**, 1046-1054.
41. E. R. Sartori, R. A. Medeiros, R. C. Rocha and O. Fatibello-Filho, *Talanta*, 2010, **81**, 1418-1424.
42. B. C. Lourencao, R. A. Medeiros, R. C. Rocha, L. H. Mazo and O. Fatibello-Filho, *Talanta*, 2009, **78**, 748-752.
43. D. K. Gosser, ed., *Cyclic Voltammetry*, VCH Publishers, New York, 1994.
44. F. Scholz, ed., *Electroanalytical Methods – Guide to Experiments and Applications*, Springer, New York, 2002.
45. M. J. G. de la Huebra, P. Hernandez, Y. Ballesteros and L. Hernandez, *Fresenius J. Anal. Chem.*, 2000, **368**, 853-856.
46. J. S. Dordevic, A. M. Kalijadis, K. R. Kumric, Z. M. Jovanovic, Z. V. Lausevic and T. M. Trtic-Petrovic, *Cent. Eur. J. Chem*, 2012, **10**, 1271-1279.

Table captions

Table 1. Comparison of the analytical parameters obtained using BDDE and PtNP-BDDE for the determination of linuron.

Electrode	Technique	LOD (μmol L^{-1})	Linear range (μmol L^{-1})	Slope (μA L mol^{-1})
BDDE	SWV	0.12	0.46 – 26.6	0.31
BDDE	DPV	0.18	0.61 – 26.0	0.67
PtNP-BDDE	SWV	0.82	2.1 – 14.9	0.35
PtNP-BDDE	DPV	0.18	0.61 – 6.6	0.70

Table 2. Comparison of the analytical parameters obtained using different electrodes and/or techniques for the determination of linuron.

Electrode	Technique	Concentration range (μmol L^{-1})	LOD (μmol L^{-1})	Reference
CPE	SWV	0.10– 1.2	0.092	[2]
Carbon fiber ultramicroelectrode	DPV	–	–	[44]
Carbon fiber microelectrode	CV	0.36–5.3	0.32	[31]
CPE/sepiolite	DPV	–	0.30	[4]
TCP-CPE	DPV	5.05 – 177	–	[3]
GCE; GCBE	DPV	5.0 – 70.0; 5.0 – 100	10.0; 6.0	[45]
BDDE	DPV	0.61 – 26.0	0.18	This work

Table 3. Addition and recovery of linuron from spiked natural water samples at a BDDE using DPV.

	Linuron / μmol L^{-1}		
Sample	Added	Found	Recovered (%)
A1	1.1	1.1 ± 0.2	100 ± 2
	3.2	3.3 ± 0.1	103 ± 1
	5.6	5.4 ± 0.1	96.4± 1
A2	1.1	1.0 ± 0.2	90.9 ± 2
	3.2	3.3 ± 0.2	103 ± 2
	5.6	5.8 ± 0.3	104 ± 2

Figure captions

Figure 1. Chemical structure of linuron.

Figure 2. Cyclic voltammograms (50 mV s^{-1}) on a BDDE for 24.0 μmol L^{-1} linuron in a BR buffer solution (pH 2.0): anodic pretreatment (dashed line) and cathodic (solid line) pretreatment.

Figure 3. Cyclic voltammograms using the cathodically pretreated BDDE for 24.0 μmol L^{-1} linuron in phosphate buffer solution at different pH values, at 50 mV s^{-1}.

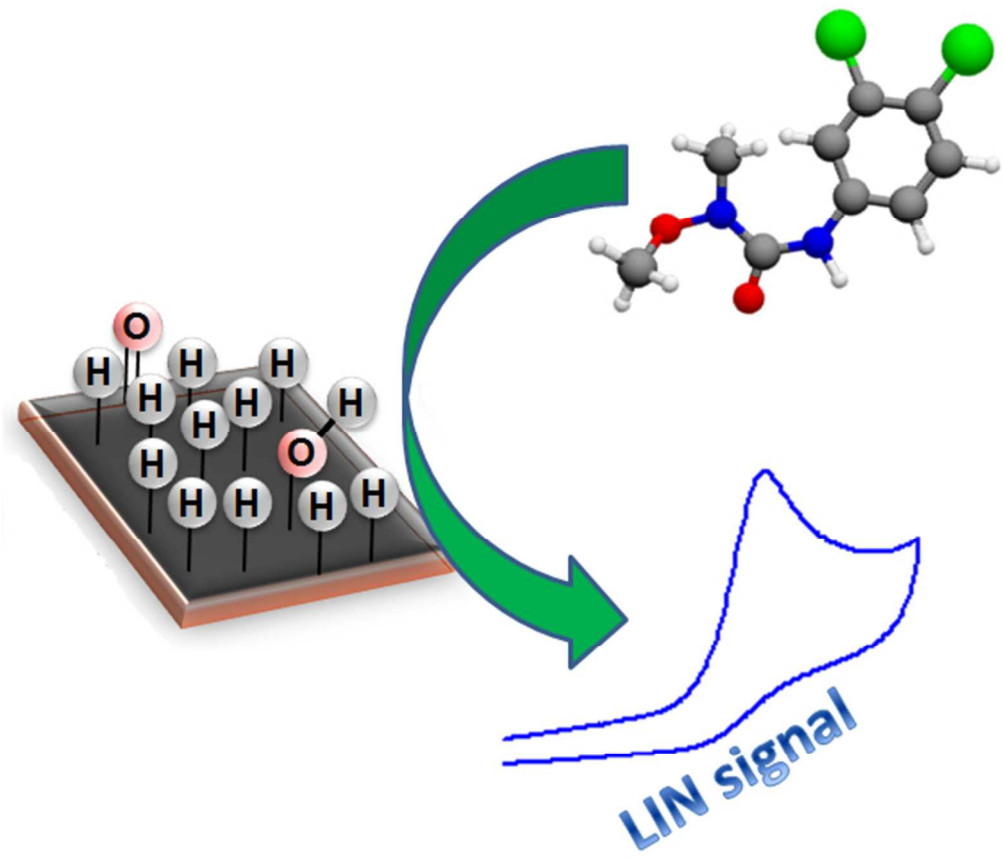
Figure 4. Cyclic voltammograms for 24.0 μmol L^{-1} linuron in 0.04 mol L^{-1} BR buffer solution (pH 2.0) obtained using a cathodically pretreated BDDE at different scan rates (ν): 5–500 mV s^{-1}. Insert: Linear dependence of log I_{ap} with $\nu^{1/2}$.

Figure 5. Proposed oxidation mechanism for linuron at the BDDE surface.

Figure 6. Differential-pulse voltammograms obtained using the cathodically pretreated BDDE for various concentration of linuron (1–13): 0.61–26.0 μmol L^{-1} in BR buffer solution (pH 2.0). Insert: Analytical curve for the linuron oxidation process.

Figure 7. MEV-FEG micrograph of BDD (A) and PtNPs onto a BDD surface, using 5 kV and magnification of 200000x.

Figure 8. Cyclic voltammograms (50 mV s^{-1}) on a BDDE (solid line) and a PtNP-BDDE (dashed line) for 30.0 μmol L^{-1} linuron in BR buffer solution (pH 2.0).



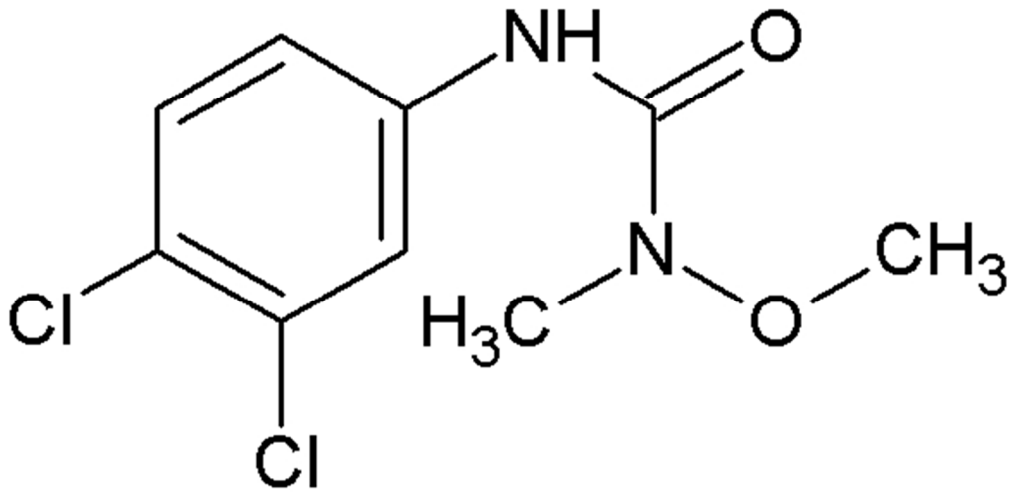


Figure 1.
49x24mm (300 x 300 DPI)

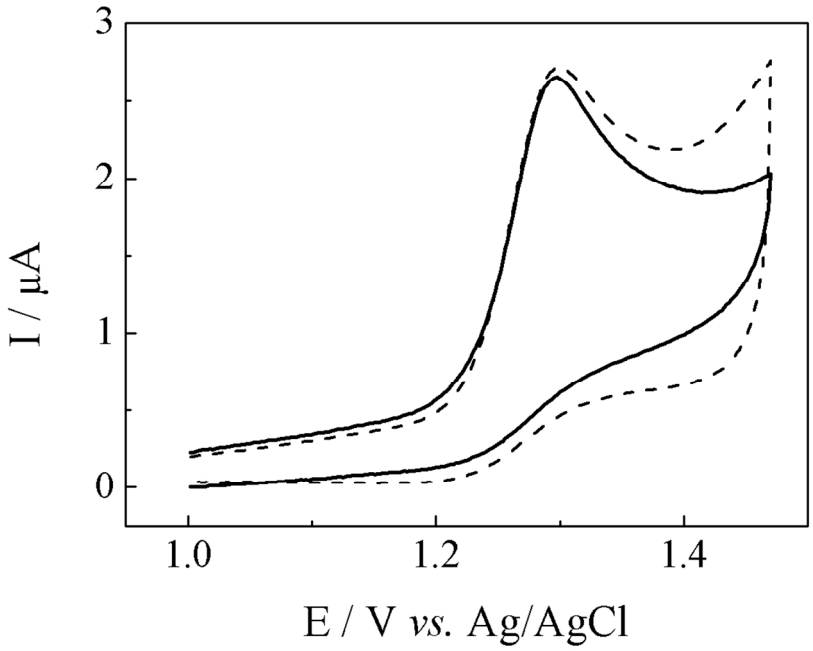


Figure 2.
116x81mm (300 x 300 DPI)

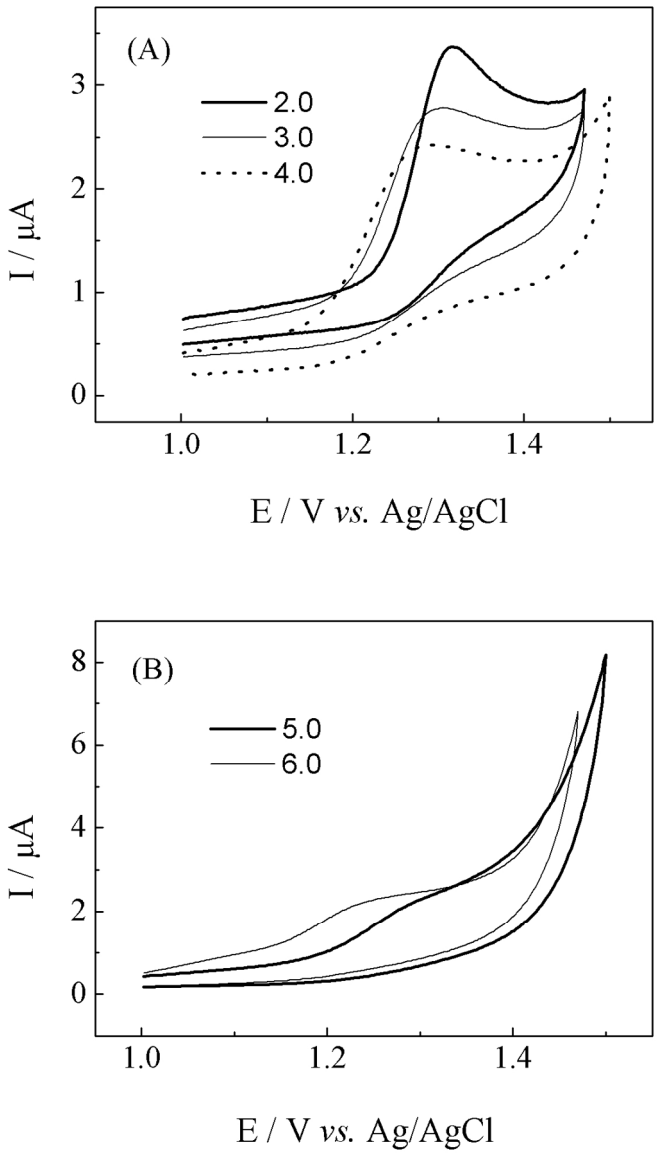


Figure 3.
118x174mm (300 x 300 DPI)

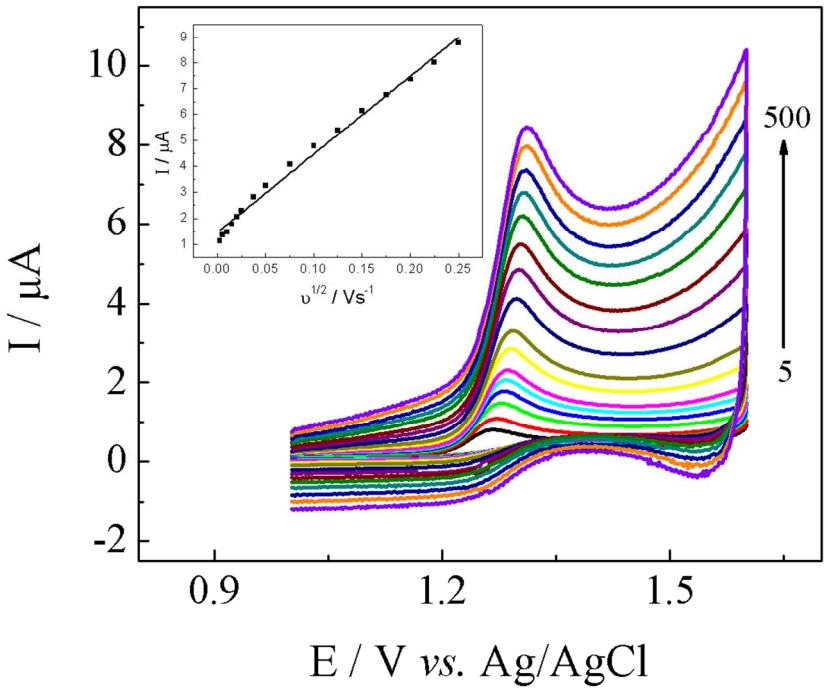
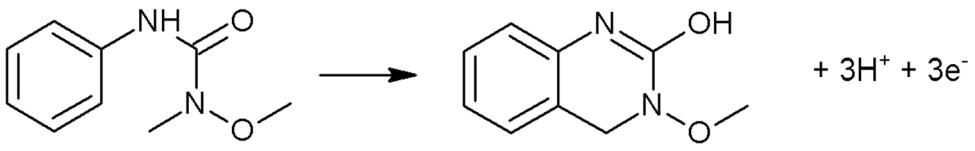


Figure 4.
111x86mm (300 x 300 DPI)



104x15mm (300 x 300 DPI)

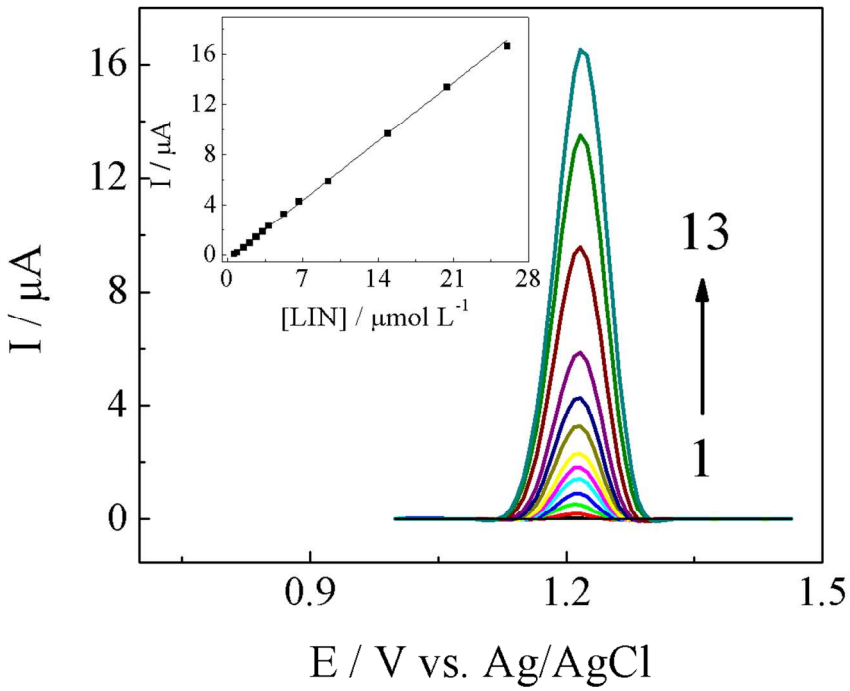


Figure 6.
111x86mm (300 x 300 DPI)

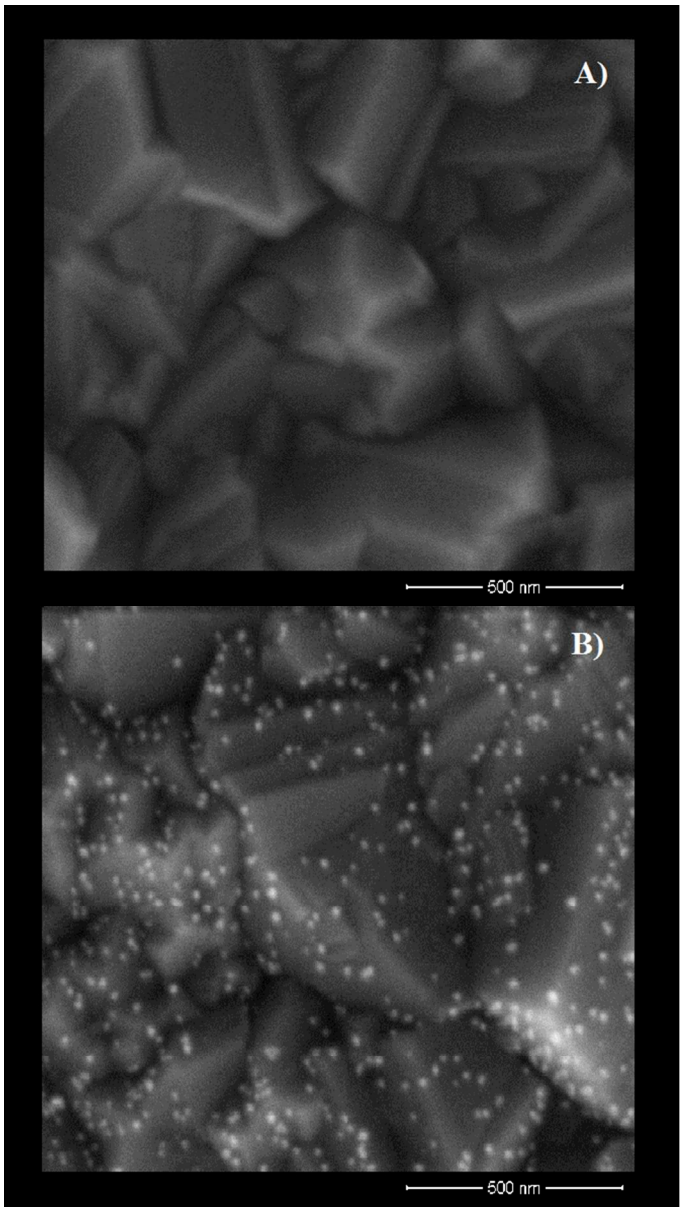


Figure 7.

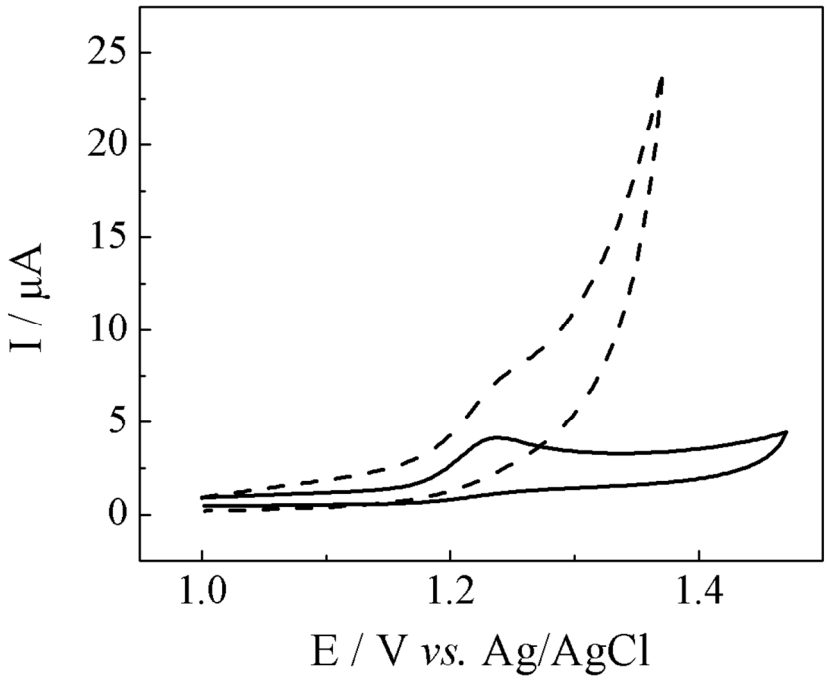


Figure 8.
111x86mm (300 x 300 DPI)