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Electrochemically pretreated zeolite-modified carbon-paste electrodes for determination of linuron in an agricultural formulation and water

L.R. Siara [a], F. de Lima [b], C.A.L. Cardoso [a], G.J. Arruda [a,*]

[a] *Chemistry Program, Universidade Estadual de Mato Grosso do Sul, Rodovia Dourados-Itahum, km 12, s/n., Caixa postal 351, Dourados, MS 79804-970, Brazil*
[b] *Institute of Chemistry, Universidade Federal de Mato Grosso do Sul, Av. Senador Filinto Muller, 1555, Caixa postal 549, Campo Grande, MS 79070-900, Brazil*

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ABSTRACT

A simple and inexpensive, yet highly sensitive electrochemical method for quantifying linuron in tap and distilled water and in agricultural formulations was developed using electrochemically pretreated zeolite-modified carbon-paste electrodes (ZMCPEs). Compared with untreated ZMCPEs, the electrochemically pretreated electrodes showed significantly enhanced peak currents for linuron oxidation. Scanning electron microscopy and energy-dispersive x-ray spectroscopy were used to examine the structure of the zeolite-modified and unmodified carbon-paste electrodes (CPEs). ZMCPEs were electrochemically characterized using cyclic voltammetry, chronocoulometry, square-wave voltammetry, and electrochemical impedance spectroscopy. A mechanism for linuron oxidation on ZMCPE surfaces was proposed. The electrochemical variables taken into account were electrode area, number of transferred electrons, electron transfer coefficient, electrode reaction standard rate constant, surface coverage, and capacitance of the electric double layer. Zeolite was found to have a strong influence on these variables. The electrochemical procedure applied to linuron was developed using electrochemically pretreated ZMCPEs under optimal conditions. Linuron oxidation currents exhibited linear concentration in the 87.36 to 625.72 nmol L^{-1} range, with a limit of detection of 22.57 nmol L^{-1}. The proposed electrochemical method was employed to quantify linuron in tap and distilled water and in a commercial agricultural formulation. Recovery rates were in the 99% to 101% range, indicating that the method can be applied to quantify linuron in these matrices. The recovery rates attained by applying the methodology developed showed high concordance with results obtained using HPLC, having a relative standard deviation of less than 1.5%.

1. Introduction

According to the International Union of Pure and Applied Chemistry (IUPAC) [1], pesticides are substances or mixtures of substances intended to prevent, destroy, or control pests, including vectors of human or animal disease, unwanted plant species, or animals causing harm or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood, wood products, or animal feedstuffs, or which may be administered to animals for the control of insects, mites, spiders, or other pests in or on their bodies. The term includes substances intended for use as plant growth regulators, defoliants, and desiccants, or to prevent premature fruit drop, as well as compounds applied to crops before or after harvesting to protect commodities against deterioration during storage or transport. Despite the benefits of pesticides, contamination from their use has become a concern for authorities, particularly in the case of food [2]. Herbicides are the largest group of chemicals used as plant protective agents. Substituted phenylureas, however, are a less dangerous class of compounds widely used as pre- and post-emergence pesticides, owing to their low toxicity to mammals, high selectivity against specific pests, and effectiveness at low dosages in common applications [3].

Phenylurea herbicides selectively control the germination of broadleaf weeds and grasses in all types of crops [4]. Because of their widespread use, control of residues in ground and surface water is crucial for embryonic and neonatal development of fish and aquatic invertebrates [5]. Linuron, or 3-[3,4-(dichlorophenyl)-1-methoxy-1-methylurea] (Scheme 1), one of the most important commercial ureas, exhibits good contact activity and the ability to kill emergent weed seedlings [6].

Pesticide analysis poses special problems, since these compounds pertain to different chemical groups, have a wide range of polarity and acidity characteristics, are present in very low

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* Corresponding author. Tel.: +55 6739022645; fax: +55 6739022661.
E-mail address: arruda@uems.br (G.J. Arruda).

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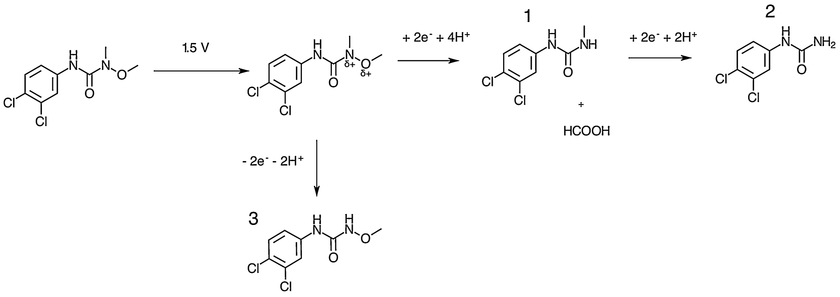

Scheme 1. Proposed mechanism of linuron oxidation.

concentrations in environmental samples, and are typically found in complex matrix samples. Improved methodologies for rapid, sensitive, accurate detection of pesticides are therefore of great interest [7,8]. Many analytical methods have been applied to the analysis of pesticides, and most are based on separation by gas or liquid chromatography [9–13]. High-performance liquid chromatography (HPLC) is preferable for phenylurea analysis [14–16]. Several sensitive, well-established chromatographic methods are reported for linuron quantification [16–19] which require expensive, complex instrumentation and involve a number of sample preparation steps and multi-step derivatization procedures. In contrast, more recent voltammetric methods are typically simple, inexpensive, and rapid, as well as sufficiently sensitive for large-scale monitoring of electrochemically active environmental pollutants [8,20].

Electrochemical studies of phenylureas, including the herbicide linuron, have employed different types of electrode materials, including carbon paste [5,21,22], mercury [23], carbon fiber [24,25], glassy carbon modified with multi-walled carbon nanotubes in the presence of unicellular green algae [26], boron-doped diamond, and glassy carbon [8]. At acidic pH values, linuron exhibits three peaks (two for oxidation, one for reduction) assigned to electrochemical reactions involving methoxy and methyl groups present in its structure. In these reactions, the methoxy group is initially replaced with a hydrogen atom, with formation of 3-(3,4-dichlorophenyl)-1-methylurea and formic acid. Subsequently, the intermediate hydroxymethyl derivative undergoes N-demethylation under oxidative conditions, with formation of 3-(3,4-dichlorophenyl)-urea and formaldehyde [22].

Following the introduction of carbon-paste electrodes (CPEs) in 1958, instrumental analysis based on electrochemical concepts underwent marked development [27]. Owing to their simple composition-essentially a mixture of carbon (graphite) powder and a binder (pasting liquid)-CPEs are among the most popular materials for laboratory preparation of electrodes, sensors, and detectors [28–30]. Since the early 1980 s, carbon-paste mixtures have been categorized into two major classes: (*i*) unmodified and (*ii*) chemically (or biologically) modified, used to produce CPEs and chemically modified carbon-paste electrodes (CMCPEs), respectively [29,31]. Zeolite-modified carbon electrodes (ZMEs) have been investigated for the physicochemical properties of zeolites, particularly ion exchange capability, molecular sieving ability, and adsorptive capacity [27–36].

In the present investigation, a new ZMCPE was developed for electrochemical quantification of linuron in tap and distilled water samples and in a commercial agricultural formulation. The modified electrodes were electrochemically characterized using cyclic voltammetry (CV), chronocoulometry, square-wave voltammetry (SWV), electrochemical impedance spectroscopy (EIS), and scanning electron microscopy (SEM). The proposed method was successfully applied to these samples.

2. Experimental

2.1. Apparatus and reagents

2.1.1. Equipment

All electrochemical measurements were performed on an Autolab PGSTAT12 instrument (Ecochemie, Utrecht, The Netherlands). The experiments were carried out in a three-electrode cell at room temperature (25 ± 1 °C), using a platinum wire as the counter-electrode, Ag/AgCl in KCl (3 mol L^{-1}) as the reference electrode, and ZMCPEs and unmodified CPEs as the working electrodes. The cell was placed in a Faraday cage to minimize background noise.

The EIS experiments, using a PGSTAT128 N potentiostat/galvanostat (Ecochemie, Utrecht, The Netherlands) equipped with a FRA2.X module, were performed at a fixed potential—namely, at an open-circuit potential (OCP) of around 0.22 V (on average) in the presence of 1 mmol L^{-1} $K_3[Fe(CN)_6]$, with potential perturbation of 25 mV (rms) within a frequency range of 10 mHz to 100 kHz.

CPEs, ZMCPEs, and zeolite samples received an ultrathin deposited gold coating to ensure visualization of their microstructures by SEM, performed on a JSM-6380LV field-emission scanning electron microscope (JEOL) equipped with an energy-dispersive X-ray spectroscopy (EDS) module. An accelerating voltage of 20 kV was applied.

CV, SWV, chronocoulometry, and EIS were used for electrochemical characterization, measurement of electric double-layer capacitance, calculation of the reactive surface area of the electrodes, and development of an analytical methodology for linuron quantification.

An HI 3221 pH meter (Hanna Instruments) equipped with a glass electrode was employed for pH adjustments. Water purified in a Milli-Q system (Waters) was used as sample for linuron quantification and to prepare the solutions.

The samples were analyzed using a 210 analytical HPLC system (Varian) equipped with a ternary module, an auto sampler, and a photodiode array detector. Star WS software (Workstation) was used to measure peak chromatogram areas. The HPLC column consisted of an RP18 (25 cm × 4.6 mm × 5 μm) reversed-phase column with a small pre-column (2.5 cm × 3 mm) containing the same packing material used to protect the analytical column. Elution was carried out with a water: acetonitrile (30:70, v:v) isocratic solvent system for 20 min. Flow rate was 1.0 mL min^{-1} and 20 μL of each sample was injected into the chromatograph. All chromatographic analyses were performed at 22 ± 1 °C.

2.1.2. Reagents and solutions

Britton-Robinson (BR) buffers in the pH range of 2.0–8.0 were prepared by adding equal volumes of boric acid (Vetec), phosphoric