Electrochimica Acta 277 (2018) 136–142

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

First electrochemistry of herbicide pethoxamid and its quantification using electroanalytical approach from mixed commercial product

Sonja Jevtić [a], Vesna Vukojević [b], Sladjana Djurdjić [b], Marija V. Pergal [c], Dragan D. Manojlović [d], Branka B. Petković [a, *], Dalibor M. Stanković [b, e]

[a] Department of Chemistry, Faculty of Natural Science and Mathematics, University of Priština, Lole Ribara 29, 38220 Kosovska Mitrovica, Serbia
[b] Innovation Center of the Faculty of Chemistry, University of Belgrade, POB 51, 118, 11158 Belgrade, Serbia
[c] Institute of Chemistry, Technology and Metallurgy, Center of Chemistry, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia
[d] Faculty of Chemistry, University of Belgrade, P.O. Box 51, 11058 Belgrade 118, Serbia
[e] The Vinca Institute of Nuclear Sciences, University of Belgrade, POB 522, 11001 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 26 March 2018
Received in revised form
30 April 2018
Accepted 1 May 2018
Available online 2 May 2018

Keywords:
Herbicide pethoxamid
Electroanalytical determination
Square wave voltammetry
River water samples
Successor T SE

ABSTRACT

This work present a new approach for the detection of relatively new herbicide pethoxamid (POA), a first electrochemical behavior and determination based on its oxidation on boron-doped diamond electrode in Britton-Robinson buffer solution at pH 4. Square wave voltammetric technique was used for quantification of POA at anodic potential of 1.35 V *vs* reference Ag/AgCl electrode. The proposed electroanalytical method is operational in the linear working range from 3 to 100 μM of POA with a limit of detection of 1.37 μM. The developed analytical procedure was successfully tested for determination of this herbicide in standard/spiked river water samples and commercial herbicide Successor T SE/spiked river water samples, offering a simple, fast and inexpensive alternative way of pesticide determining to chromatographic methods employed for this purpose.

© 2018 Published by Elsevier Ltd.

1. Introduction

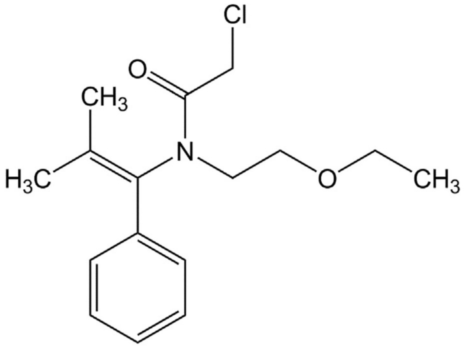
Nowadays, the chemical plant protection agents, pesticides, are indispensable in the agriculture. They assure mass production of quality food, while, on the other hand, they are one of the most serious environmental pollutants [1]. Although the development of these compounds are moving in the direction of stricter legal regulations about their monitoring and use and also designing of pesticides that fit in the concept of “ecological plant protection” (EPP) [2], still their application have a wide range of negative impacts on the environment. Agricultural soil is the first recipient of pesticides after their application, but depending of their mechanism of sorption and desorption from soil particles, pesticides can easily be transferred into the grown and surface waters and sometimes into the atmosphere, affecting the living beings, including humans [3,4]. Herbicide pethoxamid (Scheme 1), chemically named [2-chloro-N-(2-ethoxyethyl)-N-(2-phenylprop-1-enyl-2-methyl) acetamide], belongs to group of chloroacetamides. It inhibits the germination of target weeds in corn, soybeans, peas and beans, tobacco and other crops [5]. It is found that it can affects on herbicide-resistant weeds and pethoxamid received full approval for use in EU in 2006 (risk assessment in 2017) [6], while the approval for US and Canada is expected soon. Some important properties of this herbicide are high solubility in water (up to 0.4 g/L (20 °C) [5]) and almost no sorption in soils [3], so the leaching and runoff of this compound in ground and surface water is a real threat. Pethoxamid residues (and the most of other pesticides) in soil, water food and feed of plant origin usually were monitored using liquid chromatography with tandem mass spectrometry (LC–MS/MS) [6], but other analytical methods were also employed for this purpose [7]. Among reported methods, the electroanalytical methods are noted as fast and cost-effective methods for determination of these chemical agents [7,8]. Unfortunately, many of pesticides are not electroactive and that fact limits greater application of these methods.

This paper aims to application of electrochemical approach for

---

* Corresponding author.
E-mail address: branka.petkovic@pr.ac.rs (B.B. Petković).

https://doi.org/10.1016/j.electacta.2018.05.004
0013-4686/© 2018 Published by Elsevier Ltd.



Scheme 1. Structure of pethoxamid.

the determination of herbicide pethoxamid at unmodified boron-doped diamond electrode (BDDE). Some of prestigious electrochemical properties of this type of carbon electrodes are wide “potential window” with low and stable background current, corrosion resistance, high thermal conductivity and high current densities [9,10]. The BDDE overcoming the limitations of conventional carbon materials, especially in determination of, as previously thought, oxidisable organic substances such as amines, polyaromatic hydrocarbons, aminothiols, etc. [11–15]. H or O surface termination at BDDE greatly contributes to application of these electrodes to large number of organic analytes which were rarely detectable or cannot be separated from similar structure compounds at other bare carbon electrodes [9]. Nowadays, several research groups, including our, are dedicated to development of new electrochemical methods for various bioactive [16–23], polluting [24–28] and other analytes of interest [9,10] using BDDE. According to our knowledge, this is a first report of electrochemical activity of pethoxiamid and its electroanalytical sensing. This resulted in development of the simple, fast and reproductive electroanalytical procedure for determination of POA which was successfully tested on spiked surface water samples and commercial formulation.

2. Experimental

2.1. Chemicals, reagents and standard solutions

Pethoxamid, terbuthylazine, clomazone, sulcotrione and mesotrione were used as received from Sigma Aldrich. The standard solutions (10^{-3} M) of pethoxamid and clomazone were prepared in water while for other pesticides were prepared in methanol. Britton-Robinson buffer solutions (BR) (pH 2 to10) were used in electrochemical studies. Working solutions (1–100 μM, in volume of 5 mL) were freshly prepared by diluting of standard solution with BR buffer solution, pH 4. Water was purified with Millipore Simplicity 185 and analytical reagent grade chemicals were used throughout the experiments. Commercial herbicide Successor T SE, product of K&N Efthymiadis, Greece, was used in selectivity studies and real sample determinations.

Acetonitrile (>99.9%, Sigma-Aldrich HPLC grade), formic acid (Fluka analytical HPLC grade) and water (HPLC grade water, Sigma-Aldrich) were used for HPLC analysis. Syringe filters (25 mm, PTFE membrane 0.45 μm) were obtained from Agilent Technologies.

2.2. Instrumentation and measurements

Electrochemical measurements (cyclic and square wave voltammetry studies) were performed at on PalmSens 3 potentiostat/galvanostat/impedance analyzer with PSTrace software (PalmSens BV, Netherlands). Three-electrode system in the electrochemical cell was consisted from Ag/AgCl (1 M KCl) reference electrode and platinum wire counter electrode (CH Instruments, USA) while working electrode was boron-doped diamond electrode (diameter of 3 mm, a resistivity of 0.075 Ω cm and a boron doping level of 1000 ppm, product of Windsor Scientific Ltd, Slough, Berkshire, United Kingdom). In order to renew surface and provide hydrogen termination, BDDE was firstly anodically pretreated at +2 V followed by cathodic pretreatment at −2 V in 0.5 M sulfuric acid, both processes for a period of 180 s. Before every measurement, the electrode was slightly polished with piece of cotton. pH measurements were done on Hanna Instruments pH meter with combined glass electrode. All experiments were done at laboratory temperature of 20 °C.

The determination of pethoxamid and pethoxamid from Successor in surface water matrix by high-pressure liquid chromatography (HPLC) as a reference (comparative) method was performed using a Thermo Ultimate 3000 RS, with photodiode array detector (DAD) set at 240 nm. The analytical procedure was developed according to modified Knauer Application Note [29]. The chromatograph was fitted with a Hypersil Gold aQ C18 analytical column (150 mm × 3 mm, 3 μm) and column was set at 40 °C. Mobile phase consisted of 0.1% formic acid water solution as component A and acetonitrile as component B. The chromatographic elution was conducted at flow rate of 1.0 ml/min in gradient mode: 50–95% component B in 8 min, 95% component B for 3 min. Injection volume was 20 μl. Data analysis was performed with software Chromeleon 6.8 (ThermoFisher Scientific, Bremen, Germany).

2.3. Sample preparation

Water sample was collected from Serbian river Sitnica, near Priština and stored in the fridge at 6 °C. Before electrochemical determination, sample was filtered through 45 μM syringe filter, mixed with BR buffer solution, pH 4 (1:2) and then spiked with calculated amount of POA standard solution or properly diluted commercial herbicide Successor T 250 SE. Spiked samples were analyzed by square wave voltammetry (SWV) at optimal working conditions (pulse amplitude of 50 mV, frequency of 10 Hz and potential step of 5 mV) and amounts of POA were calculated from calibration curve. All measurements are done in triplicate and results are given as a mean value of these measurements.

Spiked river water samples with POA and Successor T 250 SE (without added buffer solution) were analyzed on HPLC using direct water sample injection.

3. Results and discussion

3.1. Electrochemical behavior of POA at BDDE and influence of pH

Stabile micro structure of BDD results in electrode stability at extreme cathodic and anodic potentials, high resistance to surface “poisoning” by reaction products and other present chemical species and easy regeneration of active electrode surface [9]. Bearing in mind those advantages of BDDE among other carbon or metal electrodes, cyclic voltammogram of 100 μM of POA was recorded in potential range from −1.5–2 V (Fig. 1). Electroactivity of POA was noticed, observing well-defined irreversible oxidation peak at about 1.45 V.

In order to study influence of pH on this electrochemical oxidation, CVs of the same concentration of POA were recorded in pH range from 2 to 10 in BR buffer as a supporting electrolyte (Fig. 2a). The highest and the best shaped peak was obtained at pH 4, and this pH value was selected and used for further studies. As

Download English Version:

https://daneshyari.com/en/article/6602751

Download Persian Version:

https://daneshyari.com/article/6602751

Daneshyari.com