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Voltammetric behavior, quantitative determination, and corrosion investigation of herbicide bromacil

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ABSTRACT

A boron-doped diamond electrode (BDDE) was applied for a simple, and sensitive electroanalytical determination of a fungicide, bromacil (*Bro*), using differential-pulse voltammetry (DPV). For the first time, the electrochemical oxidation of *Bro* using a BDDE at + 1.65 V *vs.* an Ag/AgCl reference electrode in Britton–Robinson (B–R) buffer, pH 2.0 was investigated. To obtain the optimum experimental conditions, the effects of the pH, modulation amplitude, modulation time and step potential were studied. Under optimum conditions, the DP voltammetric determination of *Bro* was performed in the concentration range of 5.00×10^{-6}–7.50×10^{-5} mol L^{-1} ($LOD = 1.26 \times 10^{-6}$ mol L^{-1}, $LOQ = 4.22 \times 10^{-6}$ mol L^{-1}), and the validation of the method was carried out. The developed procedure was successfully applied to determine *Bro* in a spiked river water sample by the standard addition method. To achieve valuable information regarding the electrochemical oxidation mechanism of the pesticide *Bro* on BDDE, the cyclic voltammetry (CV) technique was applied. Additionally, the influence of *Bro* on the corrosion properties of stainless steel employed to produce agricultural tools was investigated by means of electrochemical methods, *e.g.* linear polarization close to the corrosion potential for corrosion rate determination, and potentiodynamic anodic polarization to characterize the resistance to pitting corrosion. Corrosion damage was characterized by means of optical microscopy.

1. Introduction

The development of new electrode materials is one of the current trends in electrochemistry. Most of all, carbon materials have attracted great interest as electrodes for their application in the area of electroanalytical chemistry. Some of them which have been investigated as working electrodes in voltammetry are carbon paste [1–4], glassy carbon [3,5–7], screen-printed carbon [3,8,9], pyrolytic graphite electrodes [10,11], *etc.* Recently, a boron-doped diamond electrode (BDDE), as a relatively new-generation environmentally friendly electrode, represents a prospective electrode material which exhibits advantageous electrochemical properties, such as a very low and stable background current, a wide working potential window, and high current density [12,13]. Due to its excellent physical and chemical robustness [14], hardness, high thermal conductivity, and chemical inertness of the BDDE [15], it is a widely used electrode for the voltammetric analysis of various biologically active compounds [6,16–27].

At the moment, pesticides play an important role in the production and development of many crops. Although there are benefits in the use of pesticides, there have also been many problems associated with their application in the environment. Unfortunately, the pesticides do not always stay on target and they are mobile in the environment, can drift, cause harm even if they are applied properly. Due to the harmful effects of pesticides on the environment and living organisms it is important to develop sensitive analytical methods for their determination. By far, chromatographic methods are the most commonly used for the detection of pesticide residues. Nevertheless, these methods are technically demanding, time consuming, and relatively expensive. Nowadays, electrochemical methods represent an alternative to the aforementioned methods, particularly due their satisfactory sensitivity, wide linear concentration range, operation simplicity, low cost of instrumentation, possibility of miniaturization, relatively short analysis time, and suitability for real-time detection [28–30].

It is also worth noting that the use of pesticides in agriculture can be damaging for the metal parts of agricultural tools and equipment due to the fact that they may be highly corrosive [31]. Therefore, it is very important to investigate the effect of pesticides on the corrosion properties of metal substrates. The literature sources report the corrosivity of some pesticides when they are in contact with aluminum, brass, steel [31], and copper [32]. Moreover, corrosion resistance against uniform and pitting corrosion may be determined under laboratory conditions. Therefore, electrochemical methods such as linear polarization resistance and

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potentiodynamic anodic polarization [33,34] may be applied for the corrosion tests.

Bromacil (*Bro* 5-bromo-3-*sec*-butyl-6-methyluracil, CAS Reg. No. 314-40-9, Fig. 1) is one of a group of compounds called substituted uracils. *Bro* is a systemic, broad-spectrum and non-selective herbicide used for the control of annual and perennial weeds and brush [35]. The mode of action of *Bro* is to enter the plant through the root zone and move throughout the plant, inhibiting photosynthesis [36]. *Bro* was first registered as a pesticide in the U.S. in 1961, and since its discovery it has been used in a variety of agricultural and non-agricultural situations [35]. *Bro* is found in the list of priority pollutants of the US Environmental Protection Agency (US EPA) [36], and the EPA classifies *Bro* as a Group C possible human carcinogen based on increases in the incidence of liver tumors in male mice, positive trends in thyroid tumors in male rats, and, to a lesser extent, its structural activity relationship to similar compounds [36].

To date, few analytical methods have been established for the determination of *Bro*, mainly using chromatographic methods such as HPLC [37,38], LC [39] and GC [40]. Moreover, several multiresidue pesticide analysis methods have been developed and reported [41–44]. To the best of the authors' knowledge, no information about the electrochemical behavior of *Bro* has so far been reported in the literature. Therefore, for the first time, this paper describes an electrochemical approach to bromacil.

The aim of this work was to develop a procedure for the determination of *Bro* on a BDDE and methods for its DPV determination in spiked river water. Moreover, to obtain valuable information about the electrooxidation mechanism of *Bro* at BDDE, the cyclic voltammetry (CV) technique was applied. Furthermore, the effect of *Bro* on the corrosion properties of stainless steel used to produce agricultural tools was studied using several electrochemical methods (linear polarization close to the corrosion potential for corrosion rate determination, and potentiodynamic anodic polarization to characterize the resistance to pitting corrosion). The characterization of corrosion damage was also performed using optical microscopy.

2. Experimental

2.1. Electrodes, electrochemical cell and instrumentation

Differential-pulse (DPV) and cyclic voltammetry (CV) were performed with a μAutolab type II potentiostat-galvanostat (EcoChemie, Autolab B.V., Utrecht, the Netherlands) controlled by GPES software (General Purpose Electrochemical System, version 4.9) in combination with an M164 electrode stand (MTM Anko Instruments, Cracow, Poland). All measurements were provided in a three–electrode setup, where: silver/silver chloride electrode/potassium chloride (Ag/AgCl, 3.0 mol L^{-1} KCl, Mineral, Poland) and platinum wire (99.99%, Mennica Państwowa S.A., Warsaw, Poland) served as reference and counter electrodes, respectively. A commercially available boron-doped diamond electrode (BDDE) with an inner disk diameter of 3.0 mm (geometric area 7.1 mm^2, electrical resistivity of 0.075 Ω cm, B/C ratio during the deposition step of 1000 ppm, declared by Windsor Scientific Ltd., United Kingdom as the producer) was used as a working electrode. The pH measurements were carried out on an Orion Star pH meter (Model A111, Thermo Scientific, the Netherlands) with a pH electrode (type Polilyte Lab, Hamilton, Switzerland).

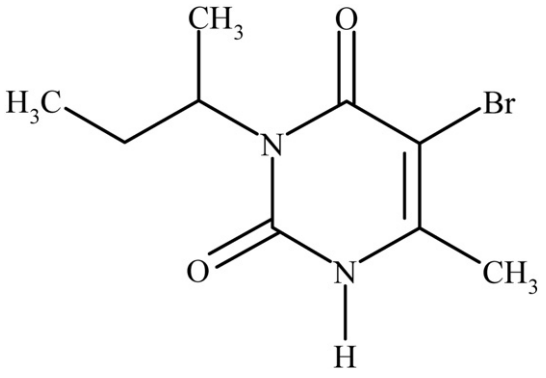

Fig. 1. Structure of *Bro*.

Corrosion studies based on electrochemical measurements were carried out using an Autolab PGSTAT 30 potentiostat-galvanostat (EcoChemie Autolab B.V., Utrecht, the Netherlands) with GPES software (version 4.9). In corrosion tests a conventional three-electrode cell assembly was used. AISI Type 316L stainless steel (Medgal, Poland) was used as a working electrode (an exposed area of 0.64 cm^2), a saturated calomel electrode (SCE, Eurosensor, Gliwice, Poland) was applied as a reference electrode, and platinum foil (99.9%, Mennica Państwowa S.A., Warsaw, Poland) was used as a counter electrode. An MMT 800BT optical microscope (mikroLAB, Lublin, Poland) was used for the characterization of corrosion damage.

2.2. Reagents and solutions

Bro (CAS No. 314-40-9, PESTANAL®, Fluka, Poland) was of 98.5% purity. A fresh *Bro* stock solution (1.0×10^{-3} mol L^{-1}) was prepared by dissolving an exact weight of the pure substance in a water–acetone mixture (9:1, *v*/*v*), and the standard solution was stored in a glass flask in a refrigerator. The changes in consistency and stability of the stock solution of *Bro* were not observed during a few weeks. Orthophosphoric acid, acetic acid, boric acid, sodium hydroxide, sulfuric acid, nitric acid, and acetone (all p.a. purity) were purchased from POCh SA (Gliwice, Poland). Britton–Robinson buffer (B–R) solutions were prepared in the usual way, *i.e.* by mixing the same concentrations (0.04 mol L^{-1}) of H_3PO_4, H_3BO_3 and CH_3COOH in water and adjusting to the desired pH value with the appropriate amount of sodium hydroxide solution (0.20 mol L^{-1}), covering the pH range of 2.0–11.0.

Sodium chloride (analytical reagent grade, POCh SA, Gliwice, Poland) was used as the corroding medium. Corrosion tests were carried out in a 3.5% solution of NaCl prepared in a water–acetone mixture (1:1, *v*/*v*), both with and without the addition of *Bro* (1.0×10^{-3} mol L^{-1}). The solutions were used without further deoxygenation.

All solutions were prepared in triply distilled water. All electrochemical measurements were carried out at laboratory temperature.

2.3. Measurements procedure

2.3.1. Voltammetric procedures

BDDE was activated at the beginning of each working day in a stirred 0.10 mol L^{-1} sulfuric acid solution by applying a potential of +2.4 V (*vs.* Ag/AgCl, 3.0 mol L^{-1} KCl) for 30 s.

Optimized DPV parameters were as follows: step potential of 10 mV, and modulation amplitude of 90 mV. In CV, the scan rate in the range from 10 mV s^{-1} to 500 mV s^{-1}, and the potential range from 0 V to +2.0 V were used.

The general voltammetric procedure to obtain the blank signal was as follows: the supporting electrolyte solutions were prepared in 10 mL volumetric flasks by measuring 1 mL of water–acetone mixture (9:1, *v*/*v*) and filling up to the mark with B–R buffer of appropriate pH. The solutions with pesticides for measurements were prepared in 10 mL volumetric flasks by measuring the proper volume of the *Bro* stock solution and filling up to the mark with B–R buffer of the required pH.

The measured signals were evaluated by subtracting the blank solution.

2.3.2. Corrosion procedures

The corrosion tests were carried out on AISI 316L stainless steel samples in the form of disks with a diameter of 16 mm and a thickness of