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Voltammetric and corrosion studies of the fungicide fludioxonil

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ABSTRACT

A new, simple, rapid, and inexpensive voltammetric method for the determination of a novel fungicide, fludioxonil (*Flu*), was firstly developed using square wave voltammetry (SWV). This was based on its electrochemical cathodic reduction at about -1.1 V vs. an Ag/AgCl/KCl reference electrode in citrate–phosphate (C–P) buffer (pH 3.7) on a renewable silver amalgam film electrode (Hg(Ag)FE). To select the optimum experimental conditions, the effect of the supporting electrolyte, pH, conditioning potential and conditioning time, frequency, amplitude, step potential, and equilibration time were studied. Under optimized conditions, the proposed method exhibited acceptable analytical performances in terms of linearity (over a concentration range from 2.00×10^{-6} to 2.25×10^{-5} mol L^{-1}), the detection limit (LOD = 5.81×10^{-7} mol L^{-1}) and the quantification limit (LOQ = 1.94×10^{-6} mol L^{-1}) for a solution containing *Flu*. The validation of the method was carried out. The developed procedure was successfully applied to determine *Flu* in the spiked Warta River water samples. To understand the *Flu* electrode mechanism, the cyclic voltammetry (CV) technique was applied. The reduction mechanism was also confirmed using mass spectrometry with the electrospray ionization (ESI–MS) technique. The influence of *Flu* on the corrosion properties of stainless steels used to produce agricultural tools were investigated using electrochemical techniques.

1. Introduction

Fludioxonil (*Flu*, CAS No. 131341–86–1, Fig. 1) is a new-generation synthetic fungicide belonging to the phenylpyrrole chemical class, which provides a broad-spectrum activity against a wide range of air-, seed- and soil-borne diseases caused by the fungi *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes* [1]. The mode of action of *Flu* is the inhibition of the transport-associated phosphorylation of glucose, as well as the prevention of glycerol synthesis [2,3]. *Flu* can be applied directly to control seeds, and also as a post–harvest treatment of fruit (stone fruit, pome fruit, pomegranate, kiwifruit, and citrus) [4].

It is extremely important to understand the environmental profile of pesticides and their metabolites to access their potential ecological impact. The monitoring of pesticide residues in the environment is one of the most important tasks facing modern analytical chemistry [5,6]. Many papers report the analytical determination of pesticides in agricultural and environmental samples. By far the most widely used methods for the detection of pesticide residues are chromatographic methods. Nevertheless, electrochemical techniques offer practical advantages, including operational simplicity, satisfactory sensitivity, a wide linear concentration range, lower equipment cost, the possibility of miniaturization, suitability for real-time detection and less sensitivity to matrix effects in comparison with separation and spectral methods [7]. Electrochemical techniques are suitable for large–scale and onsite monitoring of different electrochemically active environmental pollutants [5,8].

Flu is non-toxic to birds, bees and earthworms, but highly toxic to fish, aquatic invertebrates and algae [1]. Because *Flu* can have harmful effects on living organisms, it is important to elaborate analytical methods for its determination within the lowest possible concentration range. Therefore, different chromatographic techniques have been used, and the most common among them are high performance liquid chromatography coupled with a diode-array detector (HPLC–DAD) [2], gas chromatography coupled with nitrogen–phosphorus (GC–NPD)

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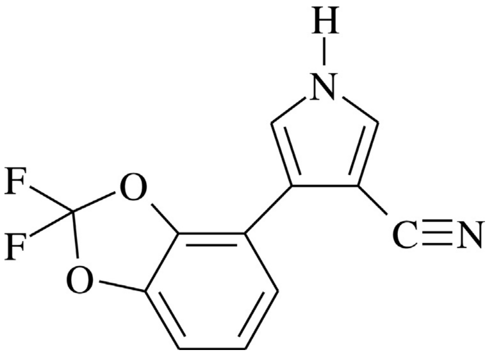

Fig. 1. Chemical structure of *Flu*.

[9] and mass spectrometry (GC–MS) detectors [3,9], and liquid chromatography/electrospray ionization–tandem mass spectrometry (LC/ESI–MS/MS) [10]. Reversed migration micellar electrokinetic chromatography (RM–MEKC) [11] is recognized as another powerful analytical technique for the determination of *Flu*.

To the best our knowledge, no information about the electrochemical behavior of *Flu* has been described in the literature. This paper is the first to report on a electrochemical study of *Flu* on a renewable silver amalgam film electrode (Hg(Ag) FE) and the appropriate method for its square wave voltammetric (SWV) determination.

Development of new electrode materials which could replace the liquid mercury due to its toxicity is of the current trends of electrochemistry. A relatively novel type of electrode, the silver amalgam film electrode (Hg(Ag)FE) constructed by scientists from AGH University of Science and Technology, Cracow, Poland, represents an appropriate alternative to the mercury electrodes. Hg(Ag)FE has been successfully used for the determination of several metals [12–18], some popular vitamins (C1, B1 and B2) [19], and a number of organic compounds [20–34].

Many commercial chemicals used in farming, including fertilizers and pesticides, may be significantly corrosive. Those elements most exposed to the corrosive effects of these chemicals are the metal parts of agricultural tools and equipment [35]. Therefore, determination of their influence on the corrosion properties of metal substrates should be done. The literature describes the corrosivity of some pesticides in contact with aluminum, brasses, steel [35] and copper [36]. This paper is the first study of the corrosion properties of *Flu*. Corrosion tests in an environment typical for these tools would be very time–consuming, therefore accelerated corrosion tests are more preferable. In an accelerated corrosion test, degradation or failure of materials are induced over a shorter period of time than under normal conditions without a change in corrosion mechanisms. Polarization or a more aggressive corrosion medium are typically used as corrosion–inducing agents.

The purpose of this study was to develop the square wave voltammetric (SWV) determination of *Flu* in the spiked Warta River water on a renewable silver amalgam film electrode (Hg(Ag) FE). Moreover, to understand the *Flu* electrode mechanism process, the cyclic voltammetric method (CV) was also applied. Furthermore, mass spectrometry with the electrospray ionization (ESI-MS) technique was used to confirm the reduction mechanism of *Flu*. Additionally, the influence of the pesticide on the corrosion properties of stainless steel employed to produce agricultural tools was investigated using several electrochemical methods, e.g. linear polarization close to E_{cor} for corrosion rate determination, and potentiodynamic anodic polarization to characterize the resistance to pitting corrosion.

2. Materials and methods

2.1. Apparatus

SWV and CV were performed in a μAutolab type II electrochemical analyzer (EcoChemie, Utrecht, The Netherlands) in combination with an M164 electrode stand (MTM Anko Instruments, Cracow, Poland). The system was run on a PC using GPES, version 4.9. A conventional three–electrode cell assembly was used consisting of a renewable silver amalgam film electrode (Hg(Ag)FE, AGH University of Science and Technology, Cracow, Poland) with a surface of 0.12 cm^2, renewed before each measurement as a working electrode, a silver/silver chloride electrode (Ag/AgCl, 3 $mol\,L^{-1}$ KCl) as a reference electrode, and a platinum wire as a counter electrode.

A CyberScan PCD 6500 pH meter (Eutech Instruments, The Netherlands) with a combined glass membrane electrode (type EPS–1, Elmetron, Poland) was used to check the pH of the solutions.

ESI–MS measurements were performed on a Varian 500–MS LC ion-trap mass spectrometer (Palo Alto, CA, USA).

Corrosion tests were carried out using an Autolab PGSTAT 30 potentiostat–galvanostat with the FRA2 module (Eco Chemie, Utrecht Netherlands) controlled by GPES, version 4.9 and FRA, version 4.9 software. Corrosion measurements were carried out in a three–electrode electrolytic cell consisting of an AISI Type 316 L Stainless Steel (Medgal, Poland) as a working electrode with an exposed area of 0.64 cm^2, a saturated calomel electrode (E° = 0.236 V *vs.* standard hydrogen electrode) as a reference electrode, and a platinum foil as a counter electrode. The corrosion damage was characterized using an optical microscope MMT 800BT (mikroLAB, Lublin, Poland).

2.2. Reagents and Solutions

All chemicals used were of analytical reagent grade (POCh SA Gliwice, Poland; Sigma-Aldrich, Poland). The analytical standard of *Flu* (Dr. Ehrenstorfer, Germany) was of 99.9% purity. A fresh *Flu* stock solution was prepared weekly at a concentration of $1 \times 10^{-3}\,mol\,L^{-1}$ by dissolving 6.20 mg of the pesticide in 25 mL of a water-acetone mixture (1:1, *v*/*v*) with the aid of an ultrasonic bath (5 min). All diluted solutions were prepared from the stock solution. Triply distilled water was used throughout. The following solutions were used with different pH values: 0.04 $mol\,L^{-1}$ Britton–Robinson (B–R) buffer solutions: $H_3BO_3 + H_3PO_4 + CH_3COOH$ – NaOH (0.2 $mol\,L^{-1}$) and citrate–phosphate (C–P) buffer solutions: $C_6H_8O_7$ (0.1 $mol\,L^{-1}$) – Na_2HPO_4 (0.2 $mol\,L^{-1}$). All electrochemical measurements were carried out at the room temperature of the laboratory (20–22 °C).

Argon (5 N, Linde gas, Poland) in electrochemical measurements was used without further purification. All solutions were stored prior to analysis in a refrigerator at 4 °C.

Methanol (Baker HPLC Analyzed, HPLC Gradient Grade) was used as a solvent in ESI–MS measurements, and helium (5 N, Linde gas, Poland) was used as the nebulizing gas.

Sodium chloride of analytical reagent grade (POCh, Poland) was used as the corroding medium. Corrosion tests were performed in a 3.5% solution of NaCl prepared in water-acetone mixture (1:1, *v*/*v*) both with and without the addition of *Flu* ($1 \times 10^{-3}\,mol\,L^{-1}$). The solutions were used in corrosion tests without further deoxygenation. Due to the temperature sensitivity of *Flu*, the solution was stored in a refrigerator and, directly prior to the corrosion test, its temperature was raised to the ambient temperature.

2.3. Measurement Procedures

2.3.1. Voltammetric procedures

The Hg(Ag)FE surface required special pretreatment before use [26,27,33,34]. Chemical treatment in 2% HNO_3 for about 5 minutes