



Study of the electrochemical stability of the difenoconazole pesticide by cyclic voltammetry and UV-Vis spectrophotometry

Research article

*Bogdan Tutunaru**, *Mioara Irina Mihai*

University of Craiova, Faculty of Sciences, Department of Chemistry, Calea București 107i, Craiova, Romania

*E-mail: tutunaruchim@yahoo.com

Received: 15.05.2024 / Accepted: 20.08.2024 / Published: 25.10.2024

Abstract

Difenoconazole is a triazole fungicide that inhibits the activity of fungi and is widely used to protect fruits, vegetables and grains. Its health and safety issues need to be further studied. In this study, experiments were conducted to investigate the degradation kinetics and electrochemical degradation pathways of difenoconazole to harmless inorganic products using two electrochemical methods; cyclic voltammetry and constant current electrolysis, in association with UV-Vis spectrophotometric analysis. The results of electrochemical tests indicated the participation of difenoconazole pesticide molecules in charge transfer processes with a priori adsorption of its molecules on the surface of the platinum electrode. UV-Vis spectrophotograms of the pesticide solution indicated a decrease in the absorbance value corresponding to difenoconazole during constant current electrolysis processes. The study elaborates on a mechanism for direct electrochemical degradation of pesticide molecules on the platinum electrode surface.

Keywords: difenoconazole, cyclic voltammetry, electrochemical stability, electrodegradation mechanism

1. INTRODUCTION

The use of pesticides in agricultural production worldwide is highly controversial and legislated as it contributes to widespread environmental pollution, noting that many current diseases can be closely linked to long-term exposure to various pesticides or pesticide residues [1-6]. Difenoconazole is a broad-spectrum triazole fungicide that inhibits cytochrome P450 (CYP450) enzyme activity, thereby inhibiting fungal growth, and plays an important role in inhibiting demethylation during ergosterol synthesis and thus preventing fungal growth and reproduction and controlling fungal diseases [3-7]. Laboratory experiments conducted to investigate the degradation kinetics, pathways, and toxicity of difenoconazole transformation products revealed certain products generated by photolysis, hydrolysis, and soil degradation, identified by UHPLC-QTOF/MS and UNIFI software. The main transformation reactions observed for difenoconazole were oxidation, dechlorination and hydroxylation in the environment [6].

Advanced oxidation processes (AOPs) refer to a wide range of pollutant removal methods, including homogeneous and heterogeneous catalytic processes and encompass electrochemical, photochemical and photoelectrochemical methods, photocatalytic oxidation, ozonation, Fenton, photo-Fenton, electro-Fenton, photo-electro-Fenton for the treatment of pollutants [8-12].

The ability of some fungi such as: *Phyllobacterium* sp., *Aeromonas* sp., *Fusarium oxysporum*, *Aspergillus oryzae*, *Lentinula edodes*, *Penicillium brevicompactum* and *Lecanicillium saksenae*, for the green biodegradation of some pesticides as well as difenoconazole, was tested [13-15].

Boron-doped diamond (BDD) electrodes were used for the electrooxidation of difenoconazole, a commonly used triazole fungicide. The observation of a maximum of the anodic current density at a potential of +1.75 V vs. Ag/AgCl may provide a basis for both the

electrochemical oxidation of difenoconazole and the development of voltammetric methods for its determination in aqueous media [16].

Removal of difenoconazole by calcium alginate composite beads [17], water treatment and ultrasound processes [18], ozone microbubbles [19] and the photo-electro Fenton method [20] indicated about 50% mineralization of the solution which contains pesticides. The correlation between the efficiency of pollutant degradation and the composition of the environment, the nature and composition of the electrodes as well as the physicochemical properties of the pollutants were taken into account.

This study aimed to evaluate the possibility of removing some active substances from the category of frequently used pesticides such as difenoconazole, through an electrochemical process of treating polluted waters. Therefore, cyclic voltammetry and constant current electrolysis in combination with UV-Vis spectrophotometric analysis were used for the electrochemical degradation of difenoconazole.

2. MATERIALS AND METHODS

2.1. *Materials*

Sodium chloride, the only supporting electrolyte used, was purchased from Merck. The fungicide difenoconazole was purchased commercially as Score 250EC in 2.5 mL vials at a concentration of 250 g L⁻¹. Two inert shiny platinum plate electrodes with a purity of 99.99% and an area of 1 cm² were used as working and auxiliary electrodes, respectively.

2.2. *Analysis methods*

The electrochemical behavior of difenoconazole pesticide was studied by cyclic voltammetry and electrolysis at a constant current density in association with UV-Vis spectrophotometry.

The electrochemical stability study of difenoconazole was performed using a VoltaLab 40 potentiostat/galvanostat, VoltaMaster 4 software. Cyclic voltammograms were recorded at a potential sweep

rate of $100 \text{ mV}\cdot\text{s}^{-1}$ in the potential range between -2.0 V ($E_{\text{start}} / E_{\text{stop}}$) and 2.0 V (E_{reverse}). In constant current electrolysis, a constant current of 50 mA was imposed for a period of 30 minutes.

Both electrochemical methods were coupled to UV-Vis spectrophotometric analysis of the working solution using a Varian Cary 50 spectrophotometer, CaryWin UV software (quartz spectrophotometric cuvette with 10 mm optical path length).

All experiments were performed at room temperature under a dynamic stirring regime at 300 rpm .

3. RESULTS AND DISCUSSION

3.1. Study of difenoconazole stability by cyclic voltammetry

Figure 1 shows the cyclic voltammograms recorded for the platinum electrode in a 0.1 M NaCl supporting electrolyte solution and in the supporting electrolyte solution containing the pesticide difenoconazole at a concentration of $1.9\cdot 10^{-6} \text{ g}\cdot\text{L}^{-1}$.

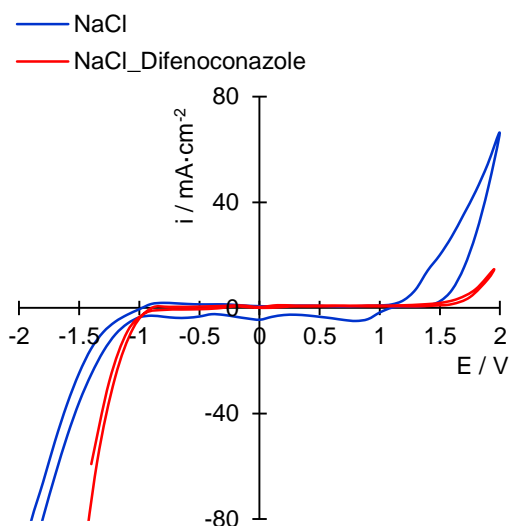


Figure 1. Cyclic voltammogram recorded on a platinum electrode in NaCl supporting electrolyte solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$) and in difenoconazole solution ($1.9\cdot 10^{-6} \text{ g}\cdot\text{L}^{-1}$) containing NaCl ($0.1 \text{ mol}\cdot\text{L}^{-1}$) as supporting electrolyte, $v = 100 \text{ mV}\cdot\text{s}^{-1}$, 100 rpm .

The comparison of the two cyclic voltammograms highlights certain particularities of the shapes of these voltammograms. Thus, corresponding to the supporting electrolyte solution, higher anodic and cathodic current densities are recorded, reaching values of 67 and -100 mA, respectively (Figure 1).

A significant increase in anodic current densities is recorded starting from a potential of 1.1 V; this charge transfer to the electrode surface is attributed to both the formation of platinum oxides on the electrode surface and the discharge of water molecules.

The cathodic polarization reveals the appearance of three maxima of the cathodic current density at potentials of 0.8, 0.0 and -0.5 V respectively, corresponding to the reduction of some oxygenated species both on the surface of the platinum electrode and in the solution (Figure 2a).

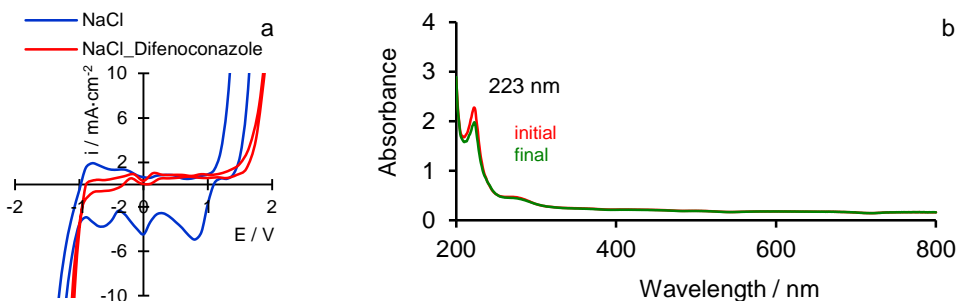


Figure 2. a) detail of cyclic voltammogram (figure 1) recorded on platinum electrode in difenconazole solution ($1.9 \cdot 10^{-6} \text{ g} \cdot \text{L}^{-1}$) containing NaCl ($0.1 \text{ mol} \cdot \text{L}^{-1}$) as supporting electrolyte, $v = 100 \text{ mV} \cdot \text{s}^{-1}$, 100 rpm; b) UV-Vis absorption spectra of difenconazole solution ($1.9 \cdot 10^{-6} \text{ g} \cdot \text{L}^{-1}$) containing NaCl ($0.1 \text{ mol} \cdot \text{L}^{-1}$) at the initial time and after cyclic voltammogram recording.

The working solution containing both the pesticide and the supporting electrolyte was analyzed by UV-Vis spectrophotometry, initially and after cyclic voltammetry. Figure 2b shows the UV-Vis spectrophotograms recorded for the working solution initially and at the end of the cyclic voltammetry. It can be seen that the initial solution leads to the recording of an absorption maximum corresponding to the wavelength of 223 nm having a higher initial relative intensity. After recording the cyclic voltammetry, the UV-Vis spectrophotogram shows a decrease in the absorption maximum, which is correlated with an

electrochemical degradation of the difenoconazole molecule during the electrode processes corresponding to the cyclic voltammetry.

The electrochemical stability of the difenoconazole pesticide was also tested by constant current electrolysis in association with UV-Vis spectrophotometry. The UV-Vis spectrophotograms of the working solution containing difenoconazole subjected to electrolysis were recorded every 2 minutes for 30 minutes, and are presented in Figure 3.

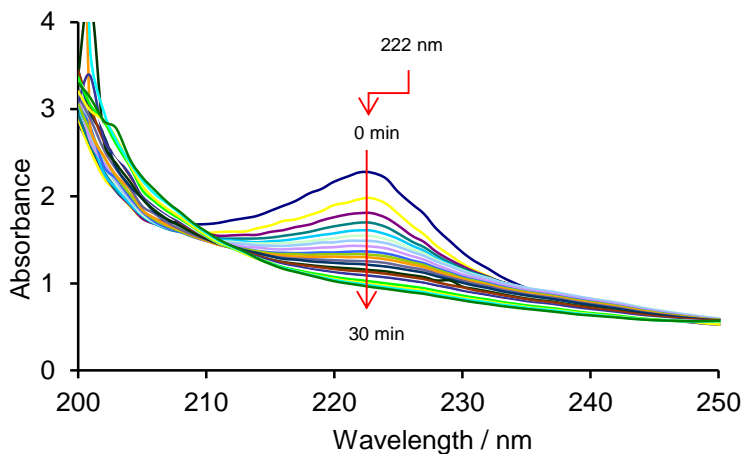


Figure 3. UV-Vis absorption spectra of difenoconazole solution ($1.9 \cdot 10^{-6} \text{ g} \cdot \text{L}^{-1}$) containing NaCl ($0.1 \text{ mol} \cdot \text{L}^{-1}$) at the initial time and after each 2 minutes of electrolysis at a constant current of 50 mA (total time = 30 mins.).

At a pesticide concentration of $1.9 \cdot 10^{-6} \text{ g} \cdot \text{L}^{-1}$, an absorption maximum in the UV range is recorded at the wavelength $\lambda = 223 \text{ nm}$ with an intensity of 2.27 (Figures 2 and 3). Under constant current electrolysis conditions ($i = 50 \text{ mA}$), there is a decrease in the initial absorbance, which attests to the electrochemical degradation of difenoconazole during electrode processes.

3.2. Study of the mechanism of direct electrochemical degradation

Figure 4 shows the molecular structure of difenoconazole and highlights its four cyclic structures (C1, C2, C3, C4).

The electrochemical degradation mechanism takes into account the successive charge transfer on the surface of the platinum electrode,

REFERENCES

- [1] J. Liu, X. Xu, A. Wu, S. Song, L. Xu, C. Xu, L. Liu and H. Kuang, *Food Bioscience*, 47 (2022) 101745.
- [2] A. J. Maldonado-Reina, R. Lopez-Ruiz, J. M. Saez, R. Romero-Gonzalez and A. Garrido Frenich, *Environmental Pollution*, 349 (2024) 123924.
- [3] M. Zhang, Z. Zhou, J. Zhang, Y. Yu, L. Sun, T. Lu and H. Qian, *Chemosphere*, 294 (2022) 133742.
- [4] X. Wang, H. Ni, W. Xu, B. Wu, T. Xie, C. Zhang, J. Cheng, Z. Li, L. Tao and Y. Zhang, *Chemosphere*, 283 (2021) 131160.
- [5] J. Sun, P. F. Xiao, X. H. Yin, G. N. Zhu and T. C. M. Brock, *Ecotoxicology and Environmental Safety*, 273 (2024) 116135.
- [6] Y. Man, M. Stenrød, C. Wu, M. Almvik, R. Holten, J. L. Clarke, S. Yuan, X. Wu, J. Xu, F. Dong, Y. Zheng and X. Liu, *Journal of Hazardous Materials*, 418 (2021) 126303.
- [7] P. Satapute and S. Jogaiah, *Chemosphere*, 286 (2022) 131694.
- [8] A. A. Z. Rodrigues, M. E. L. Ribeiro de Queiroza, A. A. Neves, A. F. de Oliveira, L. H. F. Prates, J. F. de Freitas, F. Fernandes Heleno and L. R. D'Antonino Faroni, *Food Research International*, 125 (2019) 108626.
- [9] L. Pellanda de Souza, L. R. D'Antonino Faroni, F. Fernandes Heleno, F. G. Pinto, M. E. Lopes Ribeiro de Queiroz and L. H. Figueiredo Prates, *Food Chemistry*, 243 (2018) 435–441.
- [10] M. Al Rashidi, O. El Mouden, A. Chakir, E. Roth and R. Salghi, *Atmospheric Environment*, 45 (2011) 5997-6003.
- [11] H. Lamkhanter, S. Frindy, Y. Park, M. Sillanpää and H. Mountacer, *Materials Chemistry and Physics*, 267 (2021) 124713.
- [12] M. A. Sandoval, J. Vidal, W. Calzadilla and R. Salazar, *Current Opinion in Electrochemistry*, 36 (2022) 101125.
- [13] A.P. Pinto, C. Serrano, T. Pires, E. Mestrinho, L. Dias, D. Martins Teixeira and A.T. Caldeira, *Science of the Total Environment*, 435–436 (2012) 402–410.
- [14] J. Yeon, J. H. Chung, K. Chon, J. C. Lee, K. D. Park, I. C. Park, D. Y. Kim, S. H. An, Y. Yoon and J. H. Ahn, *Applied Soil Ecology*, 177 (2022) 104541.
- [15] X. Chen, S. Peng, M. Liu, L. Wang, K. Pang, L. Zhang, Z. Cui and A. Liu, *Chemosphere*, 310 (2023) 136863.
- [16] R. Šelešovská , K. Schwarzová-Pecková, R. Sokolová , K. Krejcová and P. Martinková-Kelíšková, *Electrochimica Acta*, 381 (2021) 138260.
- [17] Q. Zhou, W. Wang, F. Liu and R. Chen, *Chemosphere*, 286 (2022) 131813.
- [18] I. Hrynko, P. Kaczynski, S. Łuniewski and B. Łozowicka, *Chemosphere*, 333 (2023) 138890.
- [19] X. Li, C. Liu, F. Liu, X. Zhang, X. Chen, Q. Peng, G. Wu and Z. Zhao, *Food Chemistry*, 441 (2024) 138293.
- [20] J. J. Inticher, L. C. Cabrera, R. E. Guimaraes, C. F. Zorzo, L. Pellenz, D. Seibert and F. H. Borba, *Journal of Environmental Chemical Engineering*, 9 (2021) 105883.