C. R. Chimie xxx (2016) 1–7

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

An investigation of tebuconazole degradation using a gold electrode

Jelena D. Lović [a, *], Dušan Ž. Mijin [b], Mića B. Jovanović [b], Olivera S. Glavaški [c], Tijana M. Zeremski [c], Slobodan D. Petrović [b], Milka L. Avramov Ivić [a]

[a] ICTM – Institute of Electrochemistry, University of Belgrade, Njegoševa 12, 11000, Belgrade, Serbia
[b] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000, Belgrade, Serbia
[c] Institute of Field and Vegetable Crops, Maksima Gorkog 30, 21000, Novi Sad, Serbia

ARTICLE INFO

Article history:
Received 6 October 2015
Accepted 29 January 2016
Available online xxxx

Keywords:
Catalytic degradation
Tebuconazole
Gold electrode
CV voltammetry
GC–MS analysis

ABSTRACT

Tebuconazole, a pesticide that presents risks for ecosystems, groundwater and human health, was degraded on a gold electrode as the catalyst in 0.05 M $NaHCO_3$ using cyclic voltammetry (CV). First, tebuconazole was characterized on the gold electrode using CV and square wave voltammetry (SWV). The gold electrode, being highly sensitive, provided linear relationships (currents *vs.* concentrations) in the range: (0.076–0.76 μmol dm^{-3}). Based on the CV measurements, the investigated process is irreversible and diffusion-controlled. The observed catalytic role of the Au electrode in the oxidation of tebuconazole and the data obtained from CV and SWV provided the experimental conditions for the degradation of tebuconazole. The degradation was performed by continuous cycling followed by gas chromatography–mass spectroscopy (GC–MS) analysis. This enabled the catalytic elimination of tebuconazole for 60 min, which promoted the use of a gold electrode as the catalyst for the degradation of environmental pollutants. The scheme of the possible mechanism of tebuconazole degradation is given.

1. Introduction

Agricultural food production consumes about 70–80% of the total pesticides used [1]. It was estimated that 99.7% of the applied pesticides are released into the environment [2]. These large amounts of pesticides could jeopardize humans and other living organisms.

Azole fungicides (imidazoles and triazoles) show activity against a broad spectrum of fungi and inhibit fungal lanosterol-14*R*-demethylase, thus preventing and curing fungal infections [3,4]. Besides agriculture usage, they can be applied in material protection (wood, concrete, paints and roofs) [5,6].

Tebuconazole (IUPAC name: (*RS*)-1-*p*-chlorophenyl-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)pentan-3-ol; Chemical Abstracts name (±)-α-[2-(4-chlorophenyl)ethyl]-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol) is a triazole fungicide (Fig. 1).

It is used to treat fungi in cereals, peanuts, oilseed rape, soya beans, grapevines, coffee, tomatoes and potatoes [7]. Tebuconazole decreases ergosterol biosynthesis, which is a key component of fungal cell membranes [8]. The half-life of tebuconazole in soil was found to be 49–610 days under aerobic conditions [9] and thus, frequent application could lead to its accumulation in soils [9]. After application, tebuconazole may be a risk for soil ecosystems, groundwater, surface water and aquatic organisms [10,11]. In addition, tebuconazole is classified as a possible human carcinogen [12]. It is one of the contaminants resistant to conventional wastewater treatment [3,5]. Due to its

* Corresponding author.
E-mail address: jlovic@tmf.bg.ac.rs (J.D. Lović).

http://dx.doi.org/10.1016/j.crci.2016.01.014
1631-0748/

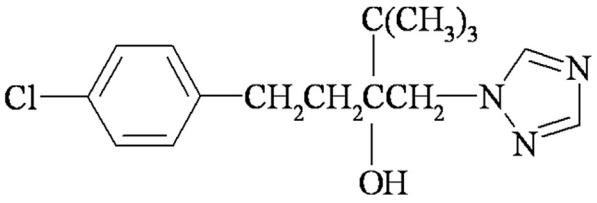

Fig. 1. Structure of tebuconazole.

persistence and the risk it poses to the environment, there is a need for the development of enhanced methods that could eliminate tebuconazole and other triazole fungicides from soil and water.

Different methods and materials have been used to remove tebuconazole from soil and water. A high-pressure mercury lamp was applied for tebuconazole photodegradation in different soils [13,14]. It was found that the photodegradation was influenced by the organic matter and clay content of the soil, as well as by soil moisture. Tebuconazole was more rapidly photodegraded under neutral than under acid and alkaline soil conditions. The degradation half-life of tebuconazole in soil is 10–22 min. A microbiological approach was also used. Screening of degrading bacteria was performed in bioreactors and the strains having the ability to degrade 51% of the initial tebuconazole concentration were identified as *Enterobacter sakazakii* and *Serratia* sp [8]. In another study, four strains that had high efficiency, high tolerance and good genetic stability were found, separated and purified from their natural environment. Their degradation efficiency for tebuconazole ranged from 89.9% to 92.2% [15]. Moreover, an invention related to the application of a glutathione-S transferase protein, prepared by cloning and recombinant production, in the degradation of tebuconazole was disclosed [16].

Advanced oxidation processes (AOP) are all characterized by the production of OH radicals and include processes such as Fenton, photo-assisted Fenton and photocatalysis [17]. Thus, the Fenton reaction was used for the treatment of an aqueous solution containing six pesticides including tebuconazole. The pesticide degradation was found to be from 60 to 100%, with mineralization up to 55% [18]. Photocatalysis was also applied for the degradation of tebuconazole. Tandem $ZnO/Na_2S_2O_8$ was used as a photosensitizer/oxidant for the photodegradation of eight pesticides including tebuconazole in leaching water at the pilot plant scale under natural sunlight [19]. TiO_2 was also used as a photocatalyst for tebuconazole degradation [5,20]. High resolution accurate mass liquid chromatography (HR-LC-MS) and gas chromatography–mass spectroscopy (GC–MS) identified nine transformation products proceeding through *tert*-butyl chain cleavage, hydroxylation, oxidation and dechlorination pathways.

Electrochemical methods are often used for pesticide degradation [21]. It should be noted that the voltammetric behavior of tebuconazole was investigated by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) using a developed mercury meniscus-modified copper solid amalgam electrode [22]. The electrochemical behavior of tebuconazole was also investigated on Bi-doped PbO_2 electrodes [23]. Another study showed that supported Ag and Au nanoparticles may be employed in sustainable environmental remediation, as they can be used at room temperature in aqueous solutions without the use of an additional stimulus, such as UV light [24]. The electrochemical behavior of tebuconazole on a gold electrode was not hitherto studied. The electrocatalytic properties of gold electrodes in the electrooxidation of numerous organic molecules are well known. For example, the oxidation of malic acid on a gold electrode proceeded in the region where the electrode was covered by gold oxide [25]. The electrochemical behavior of biological compounds, such as glucose, hormones and therapeutic drugs, was frequently investigated on gold electrodes and a layer of gold oxide formed on the surface of the gold electrode exhibited a great catalytic effect on their oxidation [25–27].

The aim of this work was the study of the catalytic influence of the surface of the gold electrode on the degradation of tebuconazole in 0.05 M $NaHCO_3$. First, tebuconazole was characterized on the gold electrode by performing CV and SWV. The data obtained were used for its quantitative determination and for the elucidation of the conditions for the catalytic elimination of tebuconazole. The products formed during the electrochemical treatment of tebuconazole were analyzed by GC–MS analysis and a possible mechanism of the degradation is proposed.

2. Materials and methods

2.1. Chemicals

Tebuconazole (purity higher than 98.8%) was supplied by DR Ehrenstorfer GmbH. All other chemicals were of p.a. grade (Merck).

2.1.1. Preparation of the electrolyte

Tebuconazole is partly soluble in water and very well soluble in alcohols. A stock solution of tebuconazole was prepared by completely dissolving 36 mg of the pesticide in 1 dm^3 of 18 MΩ cm deionized water and aliquots of this solution were taken and added to an electrochemical cell. For higher concentrations, tebuconazole is partly soluble in water and in this work the use of methanol for its dissolution was avoided.

2.2. Apparatus and preparation of electrode surfaces

Standard equipment was used for the cyclic voltammetry measurements and the three-electrode electrochemical cell was previously described in detail [27]. Polycrystalline gold (baer gold, surface area 0.5 cm^2), which served as the working electrode, was polished with diamond paste, cleaned with a mixture of 18 MΩ cm deionized water and sulfuric acid and further cleaned with 18 MΩ cm deionized water in an ultrasonic bath. A gold wire was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All potentials are given *vs.* SCE. The working electrode was checked prior to each experiment by cycling the potential scan between −0.55 and 1.0 V in the supporting solution (0.05 M $NaHCO_3$;

Please cite this article in press as: J.D. Lović, et al., An investigation of tebuconazole degradation using a gold electrode, Comptes Rendus Chimie (2016), http://dx.doi.org/10.1016/j.crci.2016.01.014