



Electrochemical degradation of triazole fungicides in aqueous solution using TiO₂-NTs/SnO₂-Sb/PbO₂ anode: Experimental and DFT studies



Weiqing Han^a, Congqiang Zhong^a, Linyue Liang^b, Yunlong Sun^a, Ying Guan^a, Lianjun Wang^{a,*}, Xiuyun Sun^a, Jiansheng Li^a

^a School of Environmental and Biological Engineering, Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu Province, China

^b Nanfang College, Nanjing Forestry University, Nanjing 210037, Jiangsu Province, China

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ABSTRACT

Triazole fungicides (TFs) are toxic and bio-refractory contaminants widely spread in environment. This study investigated electrochemical degradation of TFs in aqueous solution at TiO₂-NTs/SnO₂-Sb/PbO₂ anode with particular attention to the effect of molecular structure. Three TFs with triazole ring in one biologically treated water including tricyclazole (TC), 1H-1,2,4-triazole (Tz) and propiconazole (PPC) were selected as the target compounds. Results of bulk electrolysis showed that degradation of all TFs was fit to a pseudo first-order equation. The three compounds were degraded with the following sequence: PPC > TC > Tz in terms of their rates of oxidation. Quantum chemical calculation using the density function theory (DFT) method was combined with experimental results to describe the degradation sequence of TFs. Atom charge was calculated by DFT method and active sites of TFs were identified respectively. Analysis of intermediates by GC-MS and LC-(ESI)-MS/MS showed agreement with calculation results. In addition, the acute toxicity of TC and PPC treated solution significantly decreased after treatment by electrochemical oxidation.

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1. Introduction

Triazole fungicides (TFs) are a diverse group of commercial fungicides commonly used in vegetable, fruit, and cereal crop protection programs, and also in wood preservation and lawn care [1,2]. Chemical industry tail water represent one of the main routes of input of anthropogenic organic contaminants such as pesticides, pharmaceuticals and dyes into the environment, due to their partial to complete resistance to biodegradation during the wastewater treatment processes [3]. Three TFs with triazole ring including tricyclazole (TC), 1H-1,2,4-triazole (Tz) and propiconazole (PPC) have been identified in the biologically treated water of one industrial centralized wastewater treatment plant (CWWTP) in China. These compounds may lead to surface and groundwater contamination compromising the aquatic ecosystem and the environment [4,5]. In addition, they are toxic to plants, microorganisms, animals and humans [6,7]. In order to overcome the problem, powerful oxidation methods are required to remove potential pollutants that

cannot be degraded biologically in CWWTP for achieving their complete destruction.

In recent decades, the electrochemical oxidation of organic compounds has attracted wide attention for the treatment of toxic and persistent organic pollutants in aqueous solution because of their ability to reach the total mineralization [8–11]. Electrode material is crucial for electrochemical oxidation processes. A wide variety of electrode materials such as RuO₂ [12], SnO₂ [13], Pt [9,11], IrO₂ [14], PbO₂ [10,15–17] and BDD [18,19] electrodes have been investigated. The usage of PbO₂ anode in wastewater treatment process has received great attention because of its high efficiency, excellent mechanical and chemical resistance. Wang et al. [16] used titanium as a support for PbO₂ films with an interlayer of SnO₂-Sb₂O₃, and found that such a combination can enhance the electrochemical stability.

It is reported that nanotubular TiO₂ arrays were formed on the Ti surface by anodization method [20,21]. However, because of their low conductivity and poor electrocatalytic ability, TiO₂-NTs are not an appropriate material for electrode materials. Our previous study showed that Sb-doped SnO₂ implanted into a Ti substrate combined in a stake structure with the TiO₂-NTs can increase the chemical stability and the electrochemical catalytic activity [22]. Nevertheless, TiO₂-NTs can serve as a tubal template, and SnO₂-Sb/PbO₂ can be

* Corresponding author. Tel.: +86 025 84315941; fax: +86 025 84315941.

E-mail addresses: hwqxzh@sohu.com (W. Han), wanglj@mail.njust.edu.cn (L. Wang).

implanted into the TiO₂-NTs. It is an effective way to increase the active sites and loading amount of the electrocatalyst in the reaction progress, which may further improve the electrochemical activity of the TiO₂-NTs/SnO₂-Sb/PbO₂ anodes. This electrode allows the in-situ production of hydroxyl radicals (HO•) from water (Eqs. (1)), or hydroxide ion (Eqs. (2)) oxidation on the electrode surface at large quantities [15,17]. HO• are very powerful oxidizing agents and can able to non-selectively attack most organics until their total mineralization into CO₂, water and inorganic ions [23–25].



Chemically, TFs contain a triazole ring in their structure. Electrochemical oxidation of these compounds may produce aromatic products more toxic than the initial fungicide, so eliminate all organic pollutants present in water is required. Electrochemical oxidation of TC has been explored using Ti/SnO₂-Sb/PbO₂ anode in our previous study [15]. Urzúa et al. [26] have studied the degradation of PPC in water by electrochemical oxidation. The formation of Tz during the photocatalyzed mineralization process at UV-Irradiated TiO₂/H₂O interfaces have been studied by Natsuko et al. [27]. To the best of our knowledge, for the degradation of TFs, quantum chemical calculation combined with experimental results to describe the electrochemical degradation sequence of TFs are still absent and the mechanisms involved are not fully understood.

The aim of this work is to study electrochemical degradation mechanism of TFs in water using experimental and DFT analysis. We examined the removal of TFs including TC, Tz and PPC from its aqueous solution by electrochemical oxidation using TiO₂-NTs/SnO₂-Sb/PbO₂ anode. To better understand the mechanisms of degradation, the intermediates were not only verified experimentally, but also via quantum chemistry calculations. The toxicity reduction of TFs solution after electrochemical oxidation was also evaluated.

2. Experimental

2.1. Chemicals

TC (CAS: 41814-78-2, 5-methyl-[1,2,4]-triazole-[3,4-beta]-benzothiazole), Tz (CAS: 288-88-0, 1H-1,2,4 triazole) and PPC (CAS: 60207-90-1, 1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4 triazole) with purity >99% were purchased from Jiangsu Fengdeng Co., Ltd., Changzhou, China. All the reagents were used as received and all other chemicals, including SnCl₄, Sb₂O₃, HNO₃, Pb(NO₃)₂, NaF, NaOH, H₂SO₄, CaCl₂, NaHCO₃, MgSO₄ and KCl, were of analytical grade supplied by Jiangsu Ronghua Co., Ltd., Nanjing, China. All the solutions were prepared with high-purity water obtained from a Millipore Milli-Q system.

Reagents used for standards: 4-methyl-2-benzothiazolamine (CAS: 1477-42-5), 1-isothiocyanato-2-methyl-benzene (CAS: 614-69-7), 2,4-Dichlorobenzaldehyde (CAS: 874-42-0), 2,4-Dichlorobenzoic acid-methylester (CAS: 35112-28-8).

2.2. Preparation of TiO₂-NTs/SnO₂-Sb/PbO₂ anode

The titanium plates (99.6%) were etched in 18% HCl at 85 °C for 15 min to remove the oxide layers, and then anodized in an electrolyte (0.075 M KF, 0.075 M HF and 1 M H₂SO₄) at 20 V for 60 min. After anodization, the as-prepared TiO₂-NTs were washed with twice distilled water and annealed at 500 °C in oxygen ambient for 3 h with a heating and cooling rate of 1 °C min⁻¹ to obtained stable nanotubes. The SnO₂-Sb coating deposited onto the pretreated titanium was prepared by sol-gel technique. Afterwards, PbO₂ was

deposited on the SnO₂-Sb interlayer of the TiO₂-NTs substrate by anodization [17].

2.3. Electrochemical cell

Bulk oxidation of all TFs was performed in an undivided cylindrical vessel containing 200 mL solution under galvanostatic conditions (15 mA cm⁻²) at room temperature (20 °C). The solution was stirred by a magnetic stirring bar in the electrolysis process. The concentration of TFs solution was 0.3 mM, with 7.0 g L⁻¹ Na₂SO₄ as supporting electrolyte and at pH 7.0. TiO₂-NTs/SnO₂-Sb/PbO₂ electrode (30 mm × 60 mm) was used as anode with working geometric area of 24 cm². A stainless steel plate of the same area was used as cathode, the gap between the two electrodes was set to 15 mm. Samples were collected from the cell at various intervals for chemical analysis.

2.4. Analysis

The concentration of TFs was measured by Waters 1525 HPLC equipped with a Boston ODS (5 μm, 4.6 mm × 250 mm) column and a diode array detector at 35 °C. The mobile phase contained a mixture of methanol and water with a rate of 1 mL min⁻¹ at isocratic mode. Injection volume was 20 μL and samples were detected as collected without diluted. The methanol: water (V:V) was 50:50 for TC, 30:70 for Tz and 40:60 for PPC. The wavelength for ultraviolet (UV) detector was set at 288 nm for TC, 195 nm for Tz and 254 nm for PPC. Before analysis, the sample was filtrated through a 0.22 μm pore-size membrane filter.

The oxidation aromatic intermediates of TFs were analyzed by GC-MS. The GC-MS system consisted of a GC system (Agilent 7890A) and a MS instrument (Agilent 5975 C). The extraction was carried out three times with dichloromethane in a 250 mL separating funnel. Using nitrogen to extract further enrichment and analysed by using a 30 m (i.d. 0.25 mm) Agilent HP-5ms column.

Some intermediates were identified by Agilent 6410 LC-(ESI)-MS/MS. The column was thermostated at 35 °C. A volume of 20 μL of sample was injected. The ESI and the ion-trap analyzer MS parameters were optimized to reach the best sensitivity for intermediates.

Chemical oxygen demand (COD) was analyzed according to standard methods [28]. The pH values were measured by a Multi-parameter Meter (DZS-708, LeiCi). Carboxylic acids and inorganic anions were detected by IC (ICS 2000, Dionex).

An acute-static 48-h toxicity test was performed according to OECD Guideline 203 [29]. Zebrafish (*Danio rerio*) were exposed to wastewater samples at different concentrations (about 1.0 g fish per liter water). The results of the acute toxicity tests are expressed as EC_{50,48 h} (% V/V), the concentration responsible for the death in 50% of the tested population after exposure.

2.5. Quantum chemical calculation

To better explain the relationship between molecular structures of TFs and electrochemical oxidation pathway, a theoretical calculation of atom charge for the three TFs was carried out. Atom charge on the compounds was calculated using DFT method at the B3LYP/6-31G level.

3. Results and discussion

3.1. Bulk electrolysis

Electrochemical oxidation of all the TFs was performed at TiO₂-NTs/SnO₂-Sb/PbO₂ anode. Fig. 1a shows the evolution of substrate concentration as a function of electrolysis time. At the end of 105 min, 90.7% of TC, 81.5% of Tz and 94.7% of PPC were removed.

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