Chemosphere 90 (2013) 1387–1395

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Kinetic aspects and identification of by-products during the ozonation of bitertanol in agricultural wastewaters

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HIGHLIGHTS

- ▶ Bitertanol was easily degraded by ozonation in aqueous solutions.
- ▶ Reaction kinetic orders were determined as one for bitertanol and one for ozone.
- ▶ Kinetic rate constants appeared to be lower in diluted seed-loading solution.
- ▶ Four main ozonation by-products were identified by LC–ESI(+)–MS.

ARTICLE INFO

Article history:
Received 19 March 2012
Received in revised form 31 July 2012
Accepted 1 August 2012
Available online 20 September 2012

Keywords:
Ozone
Bitertanol
Wastewater
Seed loading solution
Oxidation products

ABSTRACT

The degradation of bitertanol by ozone treatment is investigated. Solutions of bitertanol (8.4 μg mL^{-1}) were prepared either by dissolution of the standard or by dilution of Gaucho Blé seed loading solution and then ozonated under different conditions. Evolution of the concentrations of bitertanol and its ozonation by-products in both solutions was monitored by HPLC–UV as a function of the treatment time for a concentration of 100 g m^{-3} of ozone in the inlet gas. Bitertanol degradation was found to follow a pseudo-first order reaction in both cases. However, the rate of the reaction in diluted seed loading solution was much lower (0.19 vs. 0.27 min^{-1} in standard solution) and was close to the reaction rate observed in the presence of a radical scavenger, tert-butanol (0.11 min^{-1}). Thus, it may be suggested that additives present in the seed loading solution may play the role of radical scavengers. Study of ozone concentration in the inlet gas (from 25 to 100 g m^{-3}) showed that ozone degradation is also a first-order reaction with respect to ozone. Four ozonation by-products were highlighted, collected and identified by HPLC coupled with an ion trap mass spectrometer using positive electrospray ionization mode. A degradation pathway of bitertanol was finally proposed.

1. Introduction

Seeds are constantly threatened by a wide range of pests or pathogen agents at different steps of development: germination, sowing and growth. Consequently, to prevent any disease or attack, seed producers currently treat seeds with water-based formulations containing not only insecticides, fungicides and repellents but also colorants and sticking agents. Bitertanol (see Table 1), a triazole fungicide, is currently implemented for crop protection (Gaucho Blé and Baycor) to control the development of fungal disease like scab (Schwabe and Jones, 1983), powdery mildew (Schepers, 1983), rusts (Negussie and Pretorius, 2012), blackspot, etc. Indeed, the antifungal activity of triazole compounds is expressed by the inhibition of the enzyme sterol 14α-demethylase, thus hindering the biosynthesis of ergosterol, an essential sterol for fungi membrane (Joseph-Horne and Hollomon, 1997; Georgopapadakou, 1998).

Seed treatments are usually carried out in batch or semi-batch reactors to fulfill a fast and homogeneous treatment. After application, reactors are generally rinsed with water. However, as the amount of pesticides and colorants is very high in seed loading solutions, the contamination and the colorization of the wastewater are dramatic.

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http://dx.doi.org/10.1016/j.chemosphere.2012.08.014

Consequently, to solve the problem of the pollution of agricultural wastewaters by pesticides, various treatment processes have been investigated: physical treatments (lined evaporative beds and activated carbon adsorption), chemical treatments (photolysis, hydrolysis and chemical oxidation) and biological treatment like activated sludge, biobeds and constructed wetlands (Ikehata and Gamal El-Din, 2006).

Ozonation, one of the chemical oxidation processes, has been widely investigated for the removal of pesticides (Lawrence and Cappelli, 1977; Reynolds et al., 1989; Ikehata and Gamal El-Din, 2005a, 2005b). However, to our knowledge, no process of ozonation of bitertanol has been investigated yet so far.

The present study reports the study of the degradation by ozonation of bitertanol present in a seed loading solution, with the aim to (i) focus on the decomposition of pesticide; (ii) highlight the formation of oxidation products by identifying them using mass spectrometry and (iii) propose a bitertanol degradation pathway.

2. Materials and methods

2.1. Chemicals and solvents

Pestanal grade standard of bitertanol (>98.0% purity) were purchased from Fluka (Seelze, Germany). Acetonitrile (HPLC grade) was purchased from Carlo Erba Reagents-SDS (Val de Reuil, France). Ultrapure water ($\geqslant 18$ MΩ cm resistivity) was obtained from Millipore Simplicity water system (Molsheim, France). Trifluoroacetic acid (TFA) (Reagent Plus, 99%) and tert-butanol (TBA) (puriss. p.a., ACS reagent) were supplied by Sigma–Aldrich (Seelze, Germany).

Gaucho Blé seed loading solution, containing bitertanol was supplied by Bayer Cropscience (Lyon, France). The concentration of bitertanol in the seed loading solution was 37.5 g L^{-1} but this solution also contained an insecticide, imidacloprid (at the concentration of 175 g L^{-1}), a bird repellent, anthraquinone (at the concentration of 125 g L^{-1}) but also colorants and sticking agents.

2.2. Preparation of aqueous solutions of pesticides

Bitertanol (8.4 μg mL^{-1}, ca 24.2 μM) solutions were prepared after dissolution of 16.8 mg in 2 L of ultrapure water – acetonitrile mixture (99:1, v/v). Acetonitrile was used to dissolve pesticides in the solution, as it has a low reactivity with ozone (Yao and Haag, 1991).

Ozonation in the presence of TBA was carried out by adding 1.5 g of TBA in a 2 L standard solution as TBA serves as an $^{\cdot}OH$ scavenger to inhibit hydroxyl radical reactions. TBA was chosen because its reaction with ozone is very slow ($k_{O3\text{-}TBA} = 3.0 \times 10^{-3}\ M^{-1}\ s^{-1}$) but it is assumed to react quickly with $^{\cdot}OH$ ($k_{\cdot OH\text{-}TBA} = 5.0 \times 10^{8}\ M^{-1}\ s^{-1}$) (Hoigné and Bader, 1983; Yao and Haag, 1991).

The seed loading solution was diluted in ultrapure water-acetonitrile mixture (99:1, v/v) to obtain a concentration of bitertanol of 8.4 μg mL^{-1}.

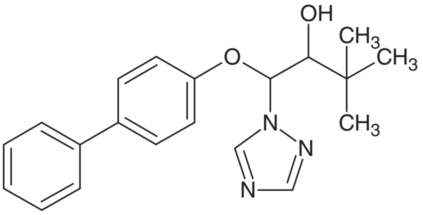
2.3. Ozonation of aqueous solutions of pesticides

A volume of 1.8 L of pesticide stock solution was placed in a 2-L semi-batch glass reactor and agitated at 400 rpm. Ozone was introduced continuously into the solution at the bottom of the reactor by bubbling a stream of ozone-oxygen mixture gas with a flow rate of 20 L h^{-1} and a concentration of ozone of 100 mg L^{-1}. Ozone was produced by Ozat CFS-1 ozone generator (Ozonia, Dubendorf, Switzerland) fed by dry pure oxygen (99.5%, Linde Gas). The inlet ozone concentration was determined at 254 nm by UV photometer (BMT 961, BMT Messtechnik, Stahnsdorf, Germany). An overpressure of 20 kPa was maintained in the reactor to increase the dissolution of ozone in the aqueous phase. Reactions were carried out at room temperature (23 °C). pH was measured before the reaction (generally between 6.0 and 6.5) and at the end of the reaction (pH 3.2–4.5). Dissolved ozone concentration was determined by the indigo colorimetric method (Bader and Hoigné, 1981) with potassium indigo trisulfonate (Sigma–Aldrich, Seelze, Germany). Effluent gases from the reactor were vented to a thermal destruction system (350 °C). Aliquots (10 mL) of ozonated solutions were collected at different treatment times from 0 to 90 min. For a semi-batch reactor fed with an ozone-oxygen mixture gas, transfer was supposed to be fast whereas ozone concentration in the liquid phase was supposed to be constant. Consequently, the limiting factor was not ozone transfer but reaction kinetic. The residual ozone was immediately quenched by bubbling pure nitrogen for 2 min to stop the reaction after withdrawal.

2.4. Analysis and fraction collection of ozonated pesticide solutions

Analysis and fraction collections of ozonated solutions were both performed thanks to an HPLC system made up of a SRD-3400 vacuum membrane degasser, an HPG-3400RS high-pressure binary pump, a WPS-3000TFC autosampler (6-port injection valve, 6-port fractionation valve) and a TCC-3000RS column compartment (Dionex, Sunnyvale, CA). Separations were performed on a Kinetex C18 analytical column (150 × 2.1 mm id, 1.7 μm particle size) from Phenomenex (Torrance, CA) protected by a Krudkatcher Ultra from Phenomenex (Torrance, CA) equipped with an integrated 0.5 μm 316 stainless steel filter element. Data acquisition and processing were carried out with the Chromeleon version 6.80 software (Dionex, Sunnyvale, CA). All components were detected by a DAD-3000RS diode-array detector (Dionex, Sunnyvale, CA) at the wavelengths of 200, 211, 254 and 270 nm. Aliquots of 20 μL were injected into the HPLC system and eluted at 50 °C, with a flow rate of 0.5 mL min^{-1} under the following gradient conditions, where *A* is 0.1% TFA in ultrapure water and B is acetonitrile: *t* = 0 min, A–B (95.1: 4.9, v/v); *t* = 18 min, A–B (95.1: 4.9, v/v);

Table 1
Chemical and physical properties of bitertanol.

Properties	Value	Structural formula for bitertanol
CAS No.	55179-31-2	
Molecular formula	$C_{20}H_{23}N_3O_2$	
Molecular weight (g mol^{-1})	337.42	
Water solubility (20–25 °C) (mg L^{-1})	3.8	
Log K_{OW} (25 °C)	4.1	
Henry's Law Constant (25 °C) (Pa m^3 mol^{-1})	8.01×10^{-11}	
Melting point (°C)	118	