ISSN 1061-9348, Journal of Analytical Chemistry, 2019, Vol. 74, No. 14, pp. 1371–1377. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Mass-spektrometriya, 2019, Vol. 16, No. 1, pp. 5–12.

ARTICLES

Photocatalytic Degradation of Chlothianidin: Effect of Humic Acids, Nitrates, and Oxygen

M. B. Kralj[a], *, E. G. Dilcan[b], G. Salihoğlu[b], D. M. Mazur[c], *, A. T. Lebedev[c], and P. Trebše[a]

[a] *Faculty of Health Sciences, University of Ljubljana, Ljubljana, 1000 Slovenia*

[b] *Faculty of Engineering, Environmental Engineering Department, Uludag University, Bursa, 16120 Turkey*

[c] *Department of Organic Chemistry, Lomonosov Moscow State University, Moscow, 119991 Russia*

**e-mail: neodmitrii@gmail.com*

Received January 17, 2018; revised February 4, 2019; accepted February 4, 2019

Abstract—The use of neonicotinoid insecticides has been constantly revised because of their impact on bees, causing their decrease and bee malady. Unfortunately, because of the worldwide differences in pesticide regulation, chlothianidin is still allowed in European Union for greenhouse use and worldwide in some cases without any restictions. Lately, it was detected on soil particles and in raw and drinking waters. The preparation of drinking waters implies different purification processes, including chlorination, ozonation, and UV irradiation and nowadays advanced oxidation processes, including TiO_2. The TiO_2 photocatalytic degradation of chlothianidin in the presence of oxygen, nitrate, and humic acids was followed by kinetic studies, whereas the photoproducts formed were identified by liquid chromatography/tandem mass spectrometry. The efficiency of different set-ups of the photocatalytic degradation of chlothianidin was evaluated by the identification of photoproducts and bioluminescence inhibition of bacteria *Vibrio fischeri*. The results indicate that less harmful photoproducts are generated in the samples with added humic acids.

Keywords: neonicotinoids, photocatalysis, TiO_2, chlothianidin, humic acid, nitrates, HPLC–MS/MS

DOI: 10.1134/S1061934819140077

INTRODUCTION

Neonicotinoids are a class of systemic insecticides used for foliar and soil tillage. Clotianidin ((E)-*N*-(2-chlorothiazol-5-ylmethyl)-*N*'-methyl-*N*''-nitroguanidine) is one of neonicotinoids, missing space, redundant space which can translocate in the xylem of plants from the soil to leaves, fruits, flowers, pollen, nectar, and plant fluid. One of undesirable consequences of the use of neonicotinoids, first reported in the case of using imidacloprid, include bee maladies [1, 2]. Currently, bees may be exposed to other neonicotinoids, such as chlothianidin, when they feed on the nectar, pollen, and guttation fluid of treated plants [3]. On a short term scale sublethal residue levels may affect foraging intensity, food consumption and orientation capability. However, honey bees can also be subjected to sublethal effects if they intensively forage on seed-dressed crop plants over longer periods [4]. Thus, in the long run, the egg-laying capacity of the queen of honey bearing bees may be seriously impaired. Experts believe that chlothianidin is one of many possible causes of a decrease in the number of bees, and the recent bee malady termed colony collapse disorder [5, 6].

The United States Environmental Protection Agency [7] (US EPA 2003) defined chlothianidin ti be from "mobile to highly mobile" compound. Clothianidin is expected to leach into groundwater, based on its persistence and ability to bind with soil particles [8]. It is usually used as a seed coating that remains stable throughout the year in soil pore water [9]. According to the published data, the half-lives of chlothianidin in soils are highly variable ranging from 17 days to several years [10]. The moisture content of soils has a positive effect on degradation rates; however, chlothianidin was observed to be more persistent than other neonicotinoids, i.e. imidacloprid and thiamethoxam, in the soil of tropical ecosystem [11]. A recent study showed that degradation of clothianidin in soils turned out to be a rather slow process with half-lives ranging from 90 (high organic carbon) to 280 (low organic carbon) days [12].

The registration and re-registration procedure for pesticides is being constantly revised. The EU Commission adopted the Rules for the complete ban of the use of imidacloprid, chlothianidin, and thiamethoxam in open air only on May 29th 2018. These data were published in the Official Journal of the European Union on May 30th 2018 [13]. According to the regulations, the use of chlothianidin in the future will be allowed only in greenhouses. However, the situation in other countries may be completely different, e.g., in China and India, which have implemented their own pesticide management systems, chlothianidin is still used because of legislation being inadequate or some-