

Monitoring the photochemical degradation of triclosan in wastewater by UV light and sunlight using solid-phase microextraction

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Abstract

Photo solid-phase microextraction (photo-SPME) is applied for the first time to study the photochemical behavior of an emerging pollutant, triclosan, in real contaminated wastewater samples using a solar simulator. In this study, water samples are extracted by SPME and then, the fiber coating is irradiated for a selected time. This on-fiber procedure, so-called photo-SPME, followed by gas chromatography–mass spectrometry makes it possible to study photodegradation kinetics and the generation of byproducts. Several photoproducts were identified in the real samples including the 2,8-dichlorodibenzo-*p*-dioxin, dichlorophenols and a compound tentatively identified as other DCDD congener or a dichlorohydroxydibenzofuran. Accordingly, it was possible to postulate main photodegradation mechanisms. Photo-SPME demonstrated slower kinetics in wastewater than in spiked ultrapure water probably due to the presence of dissolved organic matter. This technique was extensively compared with conventional aqueous photodegradation showing high similarity. The influence of pH on the triclosan photolysis and on the triclosan-dioxin conversion was also investigated in wastewater. Photodegradation of triclosan and formation of 2,8-DCDD occurred independently of sample pH. This study represents an advance in the use of photo-SPME to understand the photochemical fate of environmental organic pollutants and demonstrates its clear advantages with real samples.

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1. Introduction

The number of chemicals that nowadays can occur in the aquatic environment has increased considerably in the last decades. In this regard, a diverse group of bioactive chemicals receiving increased attention as potential environmental pollutants includes the pharmaceuticals and active ingredients in personal care products (PPCPs). These

compounds and their bioactive metabolites are continually introduced in the aquatic environment *via* a number of routes but primarily by both untreated and treated wastewater (Daughton and Ternes, 1999).

Triclosan (5-chloro-2-(2,4-dichlorophenoxy) phenol) is a widely employed antimicrobial, antibacterial and preservative agent used in many personal care products and consumer products. Due to these applications, triclosan has been identified in wastewaters (Paxéus, 1996; Agüera et al., 2003; Bester, 2003; Canosa et al., 2005; Hua et al., 2005; Thomas and Foster, 2005), superficial waters and streams (Kolpin et al., 2002; Sabaliunas et al., 2003; Kolpin

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et al., 2004; Stackelberg et al., 2004; Hua et al., 2005), and other environmental matrices (Lopez-Avila and Hites, 1980; Singer et al., 2002; Agüera et al., 2003; Boehmer et al., 2004). Initially, this compound presents low toxicity and it is partially removed during conventional wastewater treatments (Singer et al., 2002). Nevertheless, attention has been drawn to this compound due to its chemical structural similarity with highly toxic and persistent contaminants such as dioxins, and the possibility of its conversion to these hazardous compounds. Thus, the environmental fate of triclosan is a subject of special concern (Agüera et al., 2003; Latch et al., 2003; Mezcua et al., 2004; Latch et al., 2005; Rule et al., 2005).

Phototransformation processes seem to be one of the main elimination pathways of triclosan in the aquatic environment (Singer et al., 2002; Latch et al., 2005). Several authors have studied the photochemical behavior of triclosan. Kanetoshi et al. (1987, 1988) studied the photodegradation of triclosan in heterogeneous phase (1987) and in thin layer (1988), confirming its photochemical degradation and the photoformation of dichlorodibenzodioxin and trace amounts of trichlorodibenzodioxin. Ferrer et al. (2003) found that the replacement of a chlorine atom by an hydroxyl group was the preferred degradation pathway. The chlorine atom substitution by hydrogen and the cleavage of the C–O bond have also been observed by the same authors, but they did not observe the formation of DCDD in this study. Nevertheless, the formation of 2,8-DCDD as photoproduct of triclosan in water samples had been already demonstrated by Latch et al. (2003, 2005) and Mezcua et al. (2004) but only under basic-neutral pH conditions. Latch et al. (2003, 2005) investigated the role of pH and irradiation wavelength on this reaction and they observed triclosan ring closure to 2,8-DCDD in aqueous solutions buffered at pH 8 or higher, suggesting that the phenolate form of triclosan is photoreactive, whereas triclosan and its methyl ether are quite stable. Other studies have also concluded that the main photodegradation route is the direct phototransformation of the anionic phenolate form (Lindström et al., 2002; Tixier et al., 2002), although dioxin formation was not confirmed.

In summary, discrepancies on the 2,8-DCDD formation still persist, especially regarding to the pH conditions. Another subject of concern is the formation of 2,4-dichlorophenol, which is considered a USEPA priority pollutant (Latch et al., 2005).

Photo solid-phase microextraction (photo-SPME) (Lores et al., 2002; Llompert et al., 2003; Sánchez-Prado et al., 2004a,b, 2005) is a recent and very suitable analytical tool for carrying out photochemical studies of environmental organic pollutants. Recently, the authors have confirmed that direct triclosan conversion to 2,8-DCDD occurs on the polydimethylsiloxane coating of the SPME fiber (Lores et al., 2002). Nevertheless, all previous photo-SPME studies of environmental pollutants were limited to UV light and ultrapure water solutions. Therefore, the feasibility of photo-SPME in the study of the

photochemical behavior of organic compounds in real contaminated wastewater samples had not yet been demonstrated. It must be pointed out that the complexity of the matrix may affect the photoformation of some byproducts as well as their degradation–formation kinetics. Besides, from an environmental point of view, results obtained with a fixed wavelength lamp from model experiments should be confirmed using sunlight.

Thus, the present study introduces some important novelties. Photo-SPME is applied for the first time to the photodegradation study of real contaminated water samples. In addition, this technique is applied for the first time with a solar simulator photoreactor. Moreover, the samples studied here were non-spiked wastewaters with triclosan concentrations in the low ng/ml level. To our knowledge, there are some studies about photodegradation of triclosan in wastewater but they involve spiked samples and the concentrations studied were much higher than the ones usually found in real systems. In this paper, we report the results of the photochemical behavior of triclosan in wastewater using both UV and simulated sunlight. Triclosan degradation, although fast, is slower in wastewater than in ultrapure water leading to the formation of various photoproducts that were tentatively identified, including the 2,8-dichlorodibenzodioxin and several chlorophenols. Aqueous photodegradation experiments using SPME as extraction technique were also performed and compared to those obtained in photo-SPME experiments in terms of kinetics and degradation mechanisms. Furthermore, the influence of the pH was also studied, confirming dioxin formation in real samples in all cases, even at acidic pH.

2. Experimental section

Triclosan was obtained from Aldrich Chemical Company Inc. (Seelze, Germany). All reagents, analytical grade, were provided by Merck (Mollet del Vallés, Barcelona, Spain). The real wastewater samples included in this study were obtained from a sewage treatment plant located in Galicia (northwest Spain) and it corresponds to a population of approximately 100 000 inhabitants. Samples were percolated through glass fiber filters and then stored at 4 °C until being analyzed. The concentration of triclosan in these real samples was in the low ng/ml level.

Aliquots of the samples (5-ml) were placed in 10-ml glass vials and a 100 µm polydimethylsiloxane (PDMS) SPME fiber (Supelco, Bellefonte, PA) was exposed to the solution carrying out direct SPME at room temperature during 30 min with magnetic stirring. The UV-photodegradation studies were carried out in a laboratory-made photoreactor equipped with a Hg lamp (254 nm). The sunlight experiments were conducted in a Suntest CPS photosimulator (Atlas Material Testing Solutions, Chicago, IL) equipped with an air-cooled Xenon lamp (NXe 1500B, Atlas) as the radiation source. The lamp was set to medium intensity (550 W/m²). The internal temperature of the photosimulator was maintained at 35 °C. In the control

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