



# Photochemical fate and photocatalysis of 3,5,6-trichloro-2-pyridinol, degradation product of chlorpyrifos



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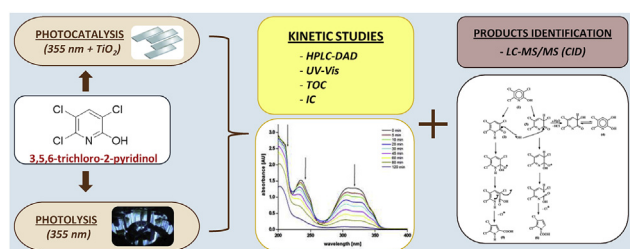
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## HIGHLIGHTS

- 3,5,6-Trichloro-2-pyridinol (TCP) is important degradation product of chlorpyrifos.
- This is the first study of photolytic and photocatalytic degradation of TCP in water.
- The identification of formed products was performed by LC-MS.
- TiO<sub>2</sub> photocatalytic study was done and evaluated in terms of mineralization rate.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this study we have focused on 3,5,6-trichloro-2-pyridinol (TCP), degradation product of chlorpyrifos. Photolysis experiments were conducted in order to elucidate its degradation mechanism. Identification of products was performed using the LC-MS technique. To evaluate the mineralization efficiency, TiO<sub>2</sub> photocatalytic study was performed. Under photolytic experimental conditions, the concentration of TCP after 120 min of irradiation reached  $5.9 \pm 1.5\%$  of the initial concentration, while chloride concentration reached approximately 73% of total chloride concentration. The TOC measurements after 120 min of photocatalytic degradation experiment revealed high mineralization rate, i.e.  $53.6 \pm 1.9\%$ , while chloride concentration reached  $26.6 \text{ mg L}^{-1}$  what means almost quantitative transformation of organic chlorine into chloride. TIC chromatogram (ESI, negative ion mode) of the reaction mixture after 30 min of irradiation revealed the presence of several peaks. One of them has already been reported previously. Two other products have been identified in this study for the first time. They have been formed by radical attack of the reactive OH<sup>•</sup> species on the carbonyl group followed by the corresponding N–C or C–C bond cleavages and recyclization with formation of the pyrrol structures substituted with carboxylic groups. Both deprotonated molecules easily lose CO<sub>2</sub> in ESI conditions.

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## 1. Introduction

Organophosphorus pesticides (OPs) have represented a group of insecticides, widely used during last three decades. Since many insecticides degrade relatively fast, some degradation products or

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metabolites may appear in agricultural products after the application in the environment or later during processing. In the literature there are many publications related to pesticides' stability, fate and behaviour in different matrices (Barceló et al., 1993; Burrows et al., 2002; Meallier, 1999), but on the other hand, not many studies have been dedicated to metabolites or degradation products in terms of their environmental fate, including physico-chemical properties, (photo)stability, bioaccumulation and toxicity.

In our study we have focused on 3,5,6-trichloro-2-pyridinol (TCP), the main hydrolytic product of chlorpyrifos, a broad-spectrum insecticide, widely used in agriculture (Liu et al., 2001; Kale et al., 1999; Dürk et al., 2008). The formation of TCP was confirmed also via chlorpyrifos photodegradation (Bavcon Kralj et al., 2007) and via its microbial degradation (Robertson et al., 1998). Available literature showed that TCP was found in green golf course leachates, where chlorpyrifos was applied in concentrations from 0.15 to 1.77 mg L<sup>-1</sup> (Shemer et al., 2005). TCP was found also in several agriculture crops such as spinach, cauliflower and potato in concentration range of mg kg<sup>-1</sup> (Randhawa et al., 2007). Moreover, TCP has been found also in urine of population in the United States (Barr et al., 2005).

For the removal of xenobiotics, released day by day into the environment, different pathways for their efficient degradation should be implemented. Ultraviolet (UV) photolysis was often used for degradation of various pesticides. Its application revealed diverse kinetics, degradation mechanisms and the formation of transformation products (TPs) (Burrows et al., 2002).

A promising approach for pesticide removal is the application of Advanced Oxidation Processes (AOPs) (Chiron et al., 2000; Konstantinou and Albanis, 2003; Badawy et al., 2006), among them heterogeneous TiO<sub>2</sub> photocatalysis (Burrows et al., 2002; Bavcon Kralj et al., 2007; Černigoj et al., 2007; Žabar et al., 2012). Studies have also showed that during AOPs more toxic products may be formed (Bavcon Kralj et al., 2007).

The previous studies of photocatalytic degradation of chlorpyrifos and chlorpyrifos-oxon, precursors of TCP, were conducted in terms of degradation kinetics, product formation, and toxicity studies (Walia et al., 1988; Barceló et al., 1993; Peñuela G. et al., 1997; Bavcon Kralj et al., 2007). The reactions follow first-order kinetics in both cases, but the degradation half-life time for chlorpyrifos-oxon was two times higher than for chlorpyrifos. Besides the formation of chlorpyrifos-oxon, during photocatalysis of chlorpyrifos, the main observed products were TCP and O,O-diethylphosphorothioate in the case of chlorpyrifos and O,O-diethylphosphate in the case of chlorpyrifos-oxon (Walia et al., 1988; Barceló et al., 1993; Peñuela G. et al., 1997; Bavcon Kralj et al., 2007). According to our knowledge the complete degradation of TCP together with the degradation mechanism has not been studied yet.

To complete the study on chlorpyrifos degradation processes we have focused on the behaviour of TCP as its main degradation product under the sunlight and on the identification of formed products using the LC-MS technique. On this basis, the degradation mechanism was proposed. The study was upgraded with the TiO<sub>2</sub> photocatalytic study and evaluated in terms of mineralisation rate.

## 2. Experimental

### 2.1. Materials

TCP, analytical standard, was provided by Fluka. Chemicals for HPLC-DAD analyses were as follows: acetic acid glacial 100% p.a. from Merck, acetonitrile, Chromasolv for HPLC, from Sigma Aldrich Company Ltd. and double deionised water (<18 MΩ cm<sup>-1</sup>) was prepared through the NANOpure water system (Barnstead, USA).

Chemicals for TOC analyses were; potassium hydrogen phthalate was from Alfa Aesar GmbH, hydrochloric acid 37% puriss. p.a. from Sigma Aldrich Company Ltd. Chemicals for ion chromatography were; sodium carbonate from Fluka, sodium bicarbonate from Fluka and Multivalent Ion chromatography Standard solution from Fluka.

### 2.2. Photolytic and photocatalytic studies

The experimental reactor consisted of a glass tube (240 mm, inner diameter 40 mm) with the effective volume of 250 mL as it is described in literature (Černigoj et al., 2006). The cell was put in the centre in-between the lamps on the distance of 10 cm. Three low-pressure mercury fluorescent lamps were used as UVA (315–400 nm) radiation source (CLEO 20 W, 438 mm × 26 mm, Philips; broad maximum at 315 nm). The photon flux in the cell was evaluated by potassium ferrioxalate actinometry (Murov et al., 1993; Hatchard and Parker, 1956), and determined to be  $2.3 \times 10^{-5}$  E L<sup>-1</sup> s<sup>-1</sup>. The temperature was kept constant during the experiment at  $28 \pm 2$  °C. The photocatalytic experiments were performed with an additional spinning basket, made entirely of Teflon, inserted into the cell. Six glass slides with the immobilised catalyst TiO<sub>2</sub> were fastened around the axis of spinning basket. Transparent TiO<sub>2</sub>-anatase films, deposited on both sides of SiO<sub>2</sub>-precoated soda-lime glass slides (175 mm × 12.5 mm × 2 mm) were produced by sol-gel processing as already described in detail in literature (Černigoj et al., 2006). The total surface area covered with TiO<sub>2</sub> was 262 cm<sup>2</sup> and the average amount of TiO<sub>2</sub> on each slide, determined by weighing (Černigoj et al., 2006), was approximately 10 mg. The reactor was rotating with the speed of 100 rpm. Aqueous solutions of TCP were prepared daily in double deionised water in concentrations for photolysis  $54.3 \pm 2.1$  mg L<sup>-1</sup> and for photocatalysis  $52.0 \pm 1.5$  mg L<sup>-1</sup>. The solutions were irradiated for fixed periods of time. The aliquots were taken periodically (0, 5, 10, 20, 30, 45, 60, 80, 120 min) and analysed with HPLC-DAD (UV Vis), UV-Vis spectrophotometer, TOC analyzer and ion chromatography. The pH was monitored using pH meter Hanna Instruments HI 8417 and its value was around 4.9.

### 2.3. Analytical procedures

#### 2.3.1. HPLC-DAD (UV-Vis) measurements and UV-Vis spectrometry

Aqueous solutions of TCP were analyzed by HPLC-DAD (UV-Vis) consisting of a Hewlett Packard 1100 Series chromatograph, coupled with a DAD detector operating in the UV-Vis range. The separation was achieved using a monolith C8 column (250 mm × 4.6 mm) with a stationary phase Chromasil 100 (end capped, pore size 5 μm) produced by BIA Separations d.o.o., Slovenia. The column thermostat was maintained at 25 °C and the injection volume was 75 μL. The eluents consisted of acetonitrile (A) and 1.5% v/v water solution of acetic acid (B); flow rate was 1 mL min<sup>-1</sup> and the wavelength was 242 nm. The gradient elution was as follows: 0 min–16 min 15% A and 85% B; 16 min–20 min 70% A and 30% B. The retention time for TCP was 18.4 min. For quantification purposes calibration from 0.1 ppm to 100 ppm with 10 different concentrations was prepared. The coefficient of determination ( $r^2$ ) was 0.9998.

The absorption spectra of TCP within irradiation time were recorded from 200 to 800 nm with the UV-Vis spectrophotometer, Hewlett Packard 8453.

#### 2.3.2. Identification of products by LC-MS

For analytic purposes we performed additional experiments by excitation within the range 296–330 nm (polychromatic light with

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