



Kinetic and mechanistic investigation of photocatalytic degradation of the N,N-diethyl-m-toluamide



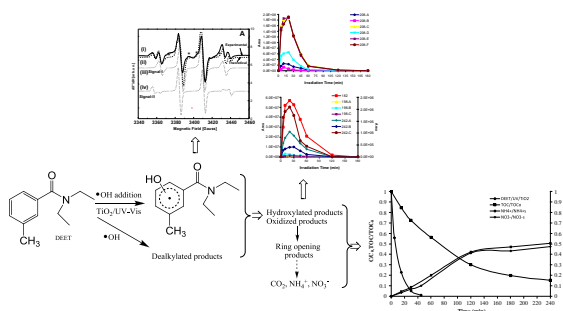
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HIGHLIGHTS

- Photocatalytic degradation and mineralization kinetics of DEET were studied.
- Degradation products were elucidated using HR-LC-MS and GC-MS techniques.
- Hydroxy-methylcyclohexadienyl radicals were detected as initial DPs by EPR.
- The acute toxicity of DEET and its TPs was assessed along photocatalytic treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Analytical and electron paramagnetic resonance (EPR) spectroscopic methods were systematically used for the kinetic and mechanistic investigation of the photocatalytic degradation of N,N-diethyl-m-toluamide (DEET), in aqueous TiO₂ suspensions under simulated solar light. The degradation of DEET followed first-order kinetics while enhanced reduction (>85%) of total organic carbon (TOC) and stoichiometric transformation of nitrogen to nitrate and ammonium ions took place after 240 min of irradiation. Numerous different structures of transformation products (TPs), with at least one isomer for the majority of them, were identified with high resolution accurate mass liquid chromatography (HR-LC-MS) and gas chromatography mass spectrometry (GC-MS). Low temperature EPR spectroscopy was used to study the photoinduced radicals created during the initial events of the photocatalytic oxidation. Two kinds of aromatic ring carbon-centered radicals i.e. hydroxy-methylcyclohexadienyl radicals have been resolved at 77 K. The second-transient conformation of the radicals is maximized after 5 min. of irradiation and then slowly decays. On the basis of identified products and radicals, a proposed pathway of photocatalytic degradation of DEET is presented, involving mono- and polyhydroxylation and/or oxidation, dealkylation and continuously the opening of the aromatic ring. Scavenging experiments indicated the contribution of ·OH as the main species in the DEET oxidation while O₂^{·-} contributes also to the degradation in a lesser extend after the initial steps of the reaction. Finally, toxicity studies based on luminescence of *Vibrio fischeri* bacteria before and after the photocatalytic treatment were also performed.

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1. Introduction

N,N-diethyl-meta-toluamide, commonly known as DEET, has been used as the active ingredient in the majority of the

commercial insect repellents for decades [1] at concentrations of 4–100% in various formulations such as lotions, creams, gels, aerosols, and sticks [2]. Its extensive usage has been related to the total protection it provides against a broad spectrum of biting insects [3]. In the last few years, contamination of DEET has been widely reported and it has been detected in various aquatic environments, including rivers, groundwater, seawater, wastewaters and even in

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drinking water treated by conventional water-treatment systems [1,4–6]. DEET can enter the environment mainly through municipal wastewater and is considered to be persistent in hydrolysis [1]. As a result of both extensive use and unintentional discharges, DEET has become an emerging contaminant and its removal from water is of high priority.

Recently, the treatment with advanced oxidation processes (AOPs) has been established as one of the most promising methods for the removal of organic contaminants from the water, avoiding the formation of toxic end products from the water. Heterogeneous photocatalysis using TiO_2 as catalyst represents an example of advanced oxidation processes, capable of achieving complete mineralization of various organic pollutants [7–9]. The detailed mechanisms for the formation of both reducing and highly oxidizing species on the surface of TiO_2 particles via a series of redox reactions are well documented in the literature [8,10,11]. Due to the complexity of the redox reactions, including also radical-induced reactions, various TPs are formed before complete mineralization is achieved. Some of these TPs can be toxic and, in some cases, more persistent than the parent compound [7,12]. Thus, a mechanistic investigation based on the identification of the TPs and the photoinduced radicals is essential for maximizing the overall process efficiency. Gas chromatography–mass spectrometry (GC–MS), liquid chromatography–mass spectrometry (LC–MS), ^1H NMR, FT-IR and EPR techniques have been widely used for the determination of organic intermediates [8].

To the best of our knowledge there is only one study dealing with the identification of photocatalytic TPs of DEET [13] using LC–MS that focused mainly on the interpretation of TPs mass spectra. The present study focuses on the detailed kinetic and mechanistic investigation of DEET photocatalytic degradation in the presence of TiO_2 under simulated solar light. Thus, the aims of the study were: (i) to evaluate the kinetics of DEET disappearance and mineralization; (ii) to identify the TPs by using a combination of powerful analytical techniques such as accurate mass HR-LC–MS, GC–MS and EPR spectroscopy; (iii) to probe the role of the reactive species in the reaction mechanism using different scavengers; (iv) to study the degradation pathways followed and (v) to evaluate the toxicity along the treatment.

2. Materials and methods

2.1. Chemicals

DEET, analytical grade (97.6%), was purchased from Sigma–Aldrich (USA). TiO_2 P25 (Degussa, Germany) was used as photocatalyst. HPLC-grade solvents (acetonitrile, isopropanol, methanol and LC-grade water) were supplied by Merck (Darmstadt, Germany). Sodium azide (NaN_3), potassium iodide (KI) and p-benzoquinone (BQ) were obtained from Sigma–Aldrich. Cellulose acetate (HA 0.45 μm) filters were supplied by Millipore (Bedford, USA). Oasis HLB (hydrophilic–lipophilic balanced copolymer of divinylbenzene/N-vinylpyrrolidone) cartridges (60 mg, 3 mL) from Waters (Mildford, MA, USA) were used for the by-products extraction. Ultrapure water was obtained from a Millipore Waters Milli-Q water purification system. Primary stock standard solution of DEET was prepared in water at a concentration of 200 mg L^{-1} and protected from light. The working solutions were further diluted from the stock solution. Calibration standards were renewed every week.

2.2. Irradiation procedures

Irradiation experiments were carried out in a Suntest XLS + apparatus (Heraeus Germany) simulating natural sunlight

irradiation. The light source was an air-cooled xenon lamp (2.2 kW) jacketed with special glass filters restricting the transmission of wavelengths below 290 nm. Irradiation experiments were performed using a cylindrical 250 mL Duran® glass UV-reactor with a flat flange lid with three necks (Lenz, Germany; 9.7 cm inner diameter, 12.8 cm external diameter, 9.5 cm reaction vessel height and 17.8 cm total height, light absorbance $\lambda < 300\text{ nm}$) with thermostatic jacket containing 250 mL of DEET aqueous solutions at near-neutral pH (pH = 6.5). Tap water cooling circuit was used to prevent any heating of the suspension, keeping the temperature at $23 \pm 1\text{ }^\circ\text{C}$. In addition, Suntest apparatus is equipped with a black standard thermometer (BST) to regulate air temperature conditions in the exposure chamber by air-cooling circuit. The irradiation was measured by a calibrated internal radiometer of the Suntest apparatus. A uniform repartition of the light within the irradiation cell is ensured by the reflectors of the instrument. The solution was mixed with the appropriate amount of catalyst and the suspension was magnetically stirred before and during the illumination. The suspension was kept in the dark for 30 min, prior to illumination to reach adsorption equilibrium onto semiconductor surface. Irradiation experiments ($I = 750\text{ W m}^{-2}$) were performed using DEET aqueous solution (10 mg L^{-1}) and 100 mg L^{-1} of TiO_2 . Initial DEET concentration of 10 mg L^{-1} was selected, in order to be high enough to facilitate identification of byproducts. The experiments were carried out using a relatively low amount of TiO_2 that enabled us to obtain slower kinetics and provided favorable conditions for the determination of reaction intermediates. Aliquots (15 mL) were withdrawn from the reactor at specific time intervals and filtered through a $0.45\text{ }\mu\text{m}$ filter to remove the TiO_2 particles.

2.3. Analytical procedures

2.3.1. Kinetic study – high performance liquid chromatography (HPLC) analysis

DEET concentrations were determined by a Dionex P680 HPLC equipped with a Dionex-100 photodiode array detector using a Discovery C₁₈, (250 mm \times 4.6 mm ID \times 5 μm) column (Supelco, Bellefonte, PA, USA). The mobile phase was a mixture of LC-grade water H_2O (50%) pH 3 (adjusted with formic acid) and acetonitrile (50%) with a flow rate of 1 mL min^{-1} . 20 μL of standard solutions and samples were injected into HPLC system. Column temperature was set at $40\text{ }^\circ\text{C}$ and DEET was detected at 210 nm. The determination of DEET concentrations was performed by a calibration curve (peak area against concentration) with seven points in the range $0.25\text{--}20\text{ mg L}^{-1}$. The linear regression equation was $y = 2.45x + 0.03$ and the coefficient of determination (R^2) was 0.9999. The detection limit was $30\text{ }\mu\text{g L}^{-1}$ using a signal-to-noise ratio (S/N) equal to 3. Finally, the relative standard error (RSE) in the determined DEET concentrations was lower than 3.5%.

2.3.2. Mineralization studies

To determine the extent of mineralization during photocatalysis, total organic carbon (TOC) were measured, by direct injection of filtered samples into a Shimadzu, TOC V-C_{SH} Analyzer using combustion catalytic oxidation non dispersive infrared method. The instrument was calibrated using total carbon standard solutions of potassium hydrogen phthalate. The RSE in the determined TOC concentrations was lower than 4.6%. The evolution of NO_3^- and NO_2^- ions, released during the oxidation of DEET, was followed by a Dionex ICS-1500 Ion Chromatography (IC) system equipped with ASRS Ultra II self-regenerating suppressor. The column was an Ion-Pac AS9-HC and the mobile phase consist of 9 mM aqueous sodium carbonate at a flow rate of 1 ml/min. 25 μL of the samples were injected into the column. The determination of NO_3^- and NO_2^- concentrations was performed using calibration curves (peak area

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